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# HUMANS

## *Organochlorine Pesticide Residues in Human Milk Samples from Women Living in Northwest and Northeast Mississippi, 1973–75* [1]

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ABSTRACT

*Organochlorine pesticide analyses were performed on human milk samples obtained from 34 women living in the Mississippi Delta, a high pesticide usage area, and from six women living in Starkville, Mississippi, a low pesticide usage area. Nine women collected samples before and after their babies had nursed so that fat levels and ΣDDT levels could be compared on whole milk and milk fat bases. ΣDDT values were independent of collection time if calculated on a milk fat basis, but not if calculated on a whole milk basis. Thus, the most consistent indicator of DDT residues were values calculated on a milk fat basis. Residue levels for p,p'-DDE, p,p'-DDT, and ΣDDT were significantly different ($P < 0.01$) in samples from the two areas. Residues of o,p'–DDT, β–BHC, and oxychlordane in milk samples from women living in the high pesticide usage area also were significantly different ($P < 0.05$). A mean value of 19.17 ppm ΣDDT, found in the milk fat of samples from the high pesticide usage area, is the highest ever reported. Samples from the low pesticide usage area contained a mean level of 2.36 ppm ΣDDT.*

### *Introduction*

During the past several years, concern about pesticides in the ecosystem has developed. Although several studies have been conducted to determine pesticide residue levels in human blood and other tissues, only recently has there been an interest in pesticide residues in human milk. Researchers have reported similar pesticide residue levels in human milk samples collected in the United States (*2, 3, 6, 9, 15, 17*), Australia (*8, 12, 13*), France (*7*), Germany (*5*), Japan (*10*), and Uruguay (*1*). Several residue levels reported in these papers were above the World Health Organization's recommended maximum concentration of 0.05 ppm ΣDDT in cow's milk. Previous work has been concerned primarily with DDT residues, but other organochlorine pesticides and their metabolites should be considered. Also, some data were reported on a whole milk basis (WB) and others were reported on a fat basis (FB); the data cannot be compared directly unless the fat content of the milk is also reported. Many studies in the United States have been conducted in areas where pesticide usage is about 0.3 kg/ha/year, which is low compared to the estimated 6.72 kg/ha/year in the agricultural areas of Mississippi.

The present study identifies and quantitates organochlorine pesticides and their metabolites in human milk from women living in the Mississippi Delta, a high pesticide usage area, and compares the levels with those found in human milk samples collected in a low pesticide use area.

The Delta is an alluvial plain which occupies most of the northwest quadrant of Mississippi. The low pesticide usage area residents were women living in Starkville, Mississippi, located in the northeast quadrant of Mississippi close to the Alabama state line. Pesticide usage in these two areas of Mississippi is quite different. The Mississippi Delta, comprised of 10 counties, produces 60 percent of the cotton, 50 percent of soybeans, and all the rice grown in Mississippi. It has been estimated that 6.72 kg (active ingredients) of all pesticides were applied per hectare of land in the Mississippi Delta in 1974, whereas only 0.27 kg/ha were applied in the area of Starkville, Oktibbeha County, Mississippi. (Robert D. Arthur, University of Mississippi, 1974: unpublished data).

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[1] Mississippi Agricultural and Forestry Experiment Station, Mississippi State, Miss. 39762, Paper No. 3297. This study was supported by the Epidemiologic Studies Program, Technical Services Division, Office of Pesticide Programs, U.S. Environmental Protection Agency, under contract No. EPA 68–02–0669.

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Concern has been expressed in the literature (*17*) over the difference in DDT levels found in human milk collected before and after a baby has nursed. Wilson et al. (17) reported respective levels of 0.15 ppm and 0.22 ppm ΣDDT in milk samples collected before and after a baby nursed. Thus in the present study authors sought the reason for the difference.

### *Sample Collection*

From 1973 to 1975, human milk samples were collected from 34 women living in the Mississippi Delta, a high pesticide usage area, and from six women living in Starkville, Mississippi, a low pesticide usage area. Nine women supplied samples collected before (fore-milk) and after (hind-milk) their babies nursed. Four of the nine women were from the high pesticide usage area.

Samples were obtained from nursing mothers who participated in the Maternal Child Health Care Program in the high pesticide usage area. The only criterion used to select donors was residence for at least five years in the established area. Samples from the low pesticide usage area were obtained from volunteers who were known to be breast feeding, who had been residing there for at least three years, and who were known to the authors. Single samples were received from each of the mothers except for the nine women who supplied both fore-milk and hind-milk samples.

Each woman expressed approximately 100 ml of milk with a clean plastic nylon breast pump which the investigators had washed with soap and water and rinsed with petroleum ether and hexane. Solvent washes were examined by gas-liquid chromatography (GLC) for contaminants; none were found. Milk was stored at −20°C in a pesticide-free glass bottle sealed with a Teflon-lined screw cap until analysis.

### *Analytical Methods*

Each milk sample was prepared and fat was determined according to the *Pesticide Analytical Manual* (*4*). Liquid-liquid partitioning and Florisil fractionation cleanup was conducted according to the *Manual of Analytical Methods* (*16*). Pesticides were identified and quantitated on a Micro-Tek MT–220 gas chromatograph with two columns having different resolution characteristics. No other confirmatory tests were used. Polychlorinated biphenyl (PCB) interference was circumvented where possible by diluting the samples and rechromatographing. When this technique was not feasible due to a low pesticide/PCB ratio, the pesticide level was corrected by subtracting interference due to PCBs. Instrument parameters and operating conditions were as follows:

| | |
|---|---|
| Columns: | (A) borosilicate glass, 6 ft × ¼ inch, packed with a mixture of 1.5 percent OV-17 and 1.95 percent QF-1 on 80–100-mesh Gas-Chrom Q |
| | (B) borosilicate glass, 6 ft × ¼ inch, packed with a mixture of 4 percent SE-30 and 6 percent QF-1 on 80–100-mesh Gas-Chrom Q |
| Detector: | electron capture, equipped with a 130 mCi tritium ionizing source |
| Temperatures: | injector 230°C<br>column 200°C<br>detector 215°C |
| Carrier gas: | prepurified nitrogen flowing at 60 ml/minute (column A) and 90 ml/minute (column B) |

Within these parameters, the sensitivity limit for aldrin was 20 pg for half scale deflection at $1.25 \times 10^{-10}$ AFS. Samples were examined specifically for the following pesticides and metabolites: *p,p′*-DDE, *o,p′*-DDE, *p,p′*-TDE, *o,p′*-TDE, *p,p′*-DDT, *o,p′*-DDT, α-BHC, β-BHC, lindane, heptachlor, heptachlor epoxide, oxychlordane, dieldrin, endrin, and mirex. Results were not corrected for recovery.

The laboratory maintained both internal and external quality assurance programs. The internal program used human milk with natural contamination and the external program used spiked fat samples which were part of a national program.

### *Statistical Methods*

Differences in fat levels in fore-milk and hind-milk samples, and changes in ΣDDT levels in milk when expressed on a whole milk basis versus a milk fat basis, were determined by use of the Student t-method of paired observations (*14*). The high pesticide and low pesticide usage area samples were compared by use of the Mann-Whitney U Test (*11*) which is a nonparametric alternative to the t-test for two independent samples.

### *Results and Discussion*

Wilson et al. (*17*) expressed concern over differences in ΣDDT levels in fore-milk and hind-milk samples. They reported ΣDDT levels of 0.15 ppm (WB) in fore-milk samples and 0.22 ppm (WB) in hind-milk samples, a significant difference ($P < 0.01$). In most nursing mammals, the hind-milk has a higher fat content than the fore-milk. Because pesticide residues are lipophilic and homogeneously distributed throughout fat, increased fat content of the milk yields increased pesticide residues in the milk. Therefore, authors felt that the difference reported by Wilson et al. (*17*) may have been due to the fat content of the milk samples. Kroger (*6*) was aware of the potential problem and analyzed samples on a fat basis.

To determine whether differences in the present study were due to the fat content, nine fore-milk and nine hind-milk samples were analyzed on a fat basis (FB). ΣDDT on a whole milk basis was then calculated by multiplying FB values times the percent fat in the sample as shown in Table 1.

Milk fat was significantly higher ($P < 0.05$) in hind-milk samples, which was reflected in ΣDDT levels re-

ported on a whole milk basis (*14*). For example, in sample No. 7 in Table 1, the fat level increased from 2.17 percent pre-nursing to 4.75 percent post-nursing. On a fat basis, ΣDDT concentrations in pre- and post-nursing samples were 3.11 ppm and 3.32 ppm, respectively, whereas ΣDDT concentrations in whole milk were 0.07 ppm and 0.15 ppm, respectively. The average difference in ΣDDT of hind-milk residues minus fore-milk residues on a fat basis was not significant, whereas the average difference in ΣDDT on a whole milk basis was significant ($P < 0.05$) (*14*). ΣDDT values are independent of collection time if reported on a fat basis, but not if reported on a whole milk basis. Therefore, the most consistent indicator of DDT residues is ppm on a fat basis. The other pesticide residues found in the samples show the same trend. From this evidence, one must conclude that the differences which Wilson et al. (*17*) reported were due to the increased fat content of the milk collected after nursing.

TABLE 1. *Comparison of ΣDDT on fat and whole milk bases in human milk samples from women living in northwest and northeast Mississippi, 1973–75*

| Sample Number | % Fat | ΣDDT, ppm | | |
|---|---|---|---|---|
| | | | Fat Basis | Whole Milk Basis[1] |
| 1 | 3.80 | B | 11.300 | 0.429 |
| | 3.60 | A | 10.680 | 0.384 |
| 2 | 5.80 | B | 20.430 | 1.185 |
| | 7.20 | A | 21.340 | 1.536 |
| 3 | 3.30 | B | 14.360 | 0.474 |
| | 2.40 | A | 16.380 | 0.393 |
| 4 | 2.20 | B | 37.620 | 0.828 |
| | 2.80 | A | 37.910 | 1.061 |
| 5 | 0.81 | B | 2.240 | 0.018 |
| | 5.50 | A | 1.580 | 0.087 |
| 6 | 2.41 | B | 3.010 | 0.073 |
| | 3.66 | A | 3.070 | 0.112 |
| 7 | 2.17 | B | 3.110 | 0.067 |
| | 4.75 | A | 3.320 | 0.153 |
| 8 | 0.75 | B | 2.470 | 0.019 |
| | 7.38 | A | 2.010 | 0.148 |
| 9 | 5.04 | B | 3.360 | 0.169 |
| | 6.18 | A | 4.250 | 0.262 |

NOTE: B = fore-milk; A = hind-milk.
[1] Calculated by multiplying fat basis values times percent fat in sample.

Residue values, extreme values, and percent positive samples of the FB milk samples collected from women in both pesticide usage areas are presented in Table 2. Ten pesticides and their metabolites were found in the milk samples. Percent positive samples varied little between the two areas for *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, α-BHC, β-BHC, lindane, heptachlor epoxide, and dieldrin, as shown in Table 2.

Savage et al. (*9*) reported similar data for percent positive samples for *p,p'*-DDE, *o,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, and β-BHC in human milk samples collected in Colorado. However, they found dieldrin in 45 percent of the samples and heptachlor epoxide in 25 percent of the samples. In the present study both residues were found in all samples collected from the high pesticide usage area. PCB residues were reported in 20 percent of the Colorado samples (*9*). Most of the samples from the Mississippi Delta contained PCBs, but no attempt was made to quantitate them. No residues of *o,p'*-DDE, *o,p'*-TDE, α-BHC, heptachlor, endrin, or mirex were found in any of the samples analyzed in the present investigation. Mean values of all pesticide residues were higher in samples from the Mississippi Delta than in samples from the low pesticide usage area, although some differences were quite small.

A comparison in Table 2 of samples from the high pesticide usage area with samples from the low pesticide usage area on the fat basis shows that *p,p'*-DDE, *p,p'*-DDT, and ΣDDT were significantly different ($P < 0.01$). Residues of *o,p'*-DDT, β-BHC, and oxychlordane in milk samples from the high pesticide usage area were significantly different ($P < 0.05$). Average levels of *p,p'*-TDE, α-BHC, heptachlor epoxide, lindane, and dieldrin were not significantly different between the two groups.

Table 3 shows the same residue values as Table 2 but expressed on a ppm whole milk basis. Again values for milk samples from the high pesticide usage area were higher than values for samples from the low pesticide usage area. The mean ΣDDT residue for samples from the high pesticide usage area was 19.17 ppm (FB) and 0.69 ppm (WB). Kroger (*6*) analyzed 53 samples from the Philadelphia, Pennsylvania, area and found ΣDDT levels of 2.40 ppm (FB). Wilson et al. (*17*) analyzed 138 samples from different areas of the United States and found a mean of 0.17 ppm ΣDDT (WB). Human milk samples from Colorado (*9*), Atlanta, Georgia (*2*), and Texas (*3*) contained ΣDDT levels of 0.06–0.12 ppm (WB). Pesticide levels in those studies were similar to levels found in the milk from the low pesticide usage area sampled in the present study. None of the previous studies reported residue values as high as those detected in the high pesticide usage area of the present study. Also, except for 12 samples in the Texas study (*3*), all samples in previous studies were collected in areas of low pesticide usage. The 12 Texas samples were collected in an agricultural area with high pesticide usage, but contained only 0.14 ppm *p,p'*-DDE plus *p,p'*-DDT (WB) (*3*). Strassman and Kutz (*15*) analyzed 57 samples from selected rice-growing counties in Arkansas and Mississippi. They found ΣDDT equivalent levels to be 0.344 ppm (WB).

ΣDDT levels of 0.06–0.43 ppm (WB) have been found in human milk in Germany (*5*), Japan (*10*), Uruguay (*12*), and Australia (*13*). Luquet et al. (*7*) from France reported finding an average of 3.24 ppm ΣDDT (FB). Miller and Fox (*8*) compared human milk samples from urban and rural areas of Australia. ΣDDT levels in the rural area were 3.17–30.90 ppm with a mean of 16.90 ppm (FB); the range of ΣDDT in the urban area was 3.26–21.00 ppm with a mean of 8.60 ppm (FB). In the rural area of Australia, large amounts of pesticides were used on tobacco. The residue values

TABLE 2. *Organochlorine pesticide residues in human milk, on a ppm fat basis, from women living in northeast and northwest Mississippi, 1973–75*

| Residue | High Pesticide Usage Area | | | | Low Pesticide Usage Area | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean[1] | Minimum | Maximum | % Positive Samples | Mean[1] | Minimum | Maximum | % Positive Samples |
| *p,p'*-DDE | 14.67 ± 2.59[2] | 2.46 | 73.83 | 100 | 1.920 ± 0.160 | 1.47 | 2.45 | 100 |
| *p,p'*-TDE | 0.04 ± 0.02 | 0 | 0.43 | 31.6 | 0.002 ± 0.002 | 0 | 0.01 | 16.7 |
| *o,p'*-DDT | 0.21 ± 0.04[2] | 0 | 1.08 | 97.4 | 0.050 ± 0.020 | 0.02 | 0.14 | 100 |
| *p,p'*-DDT | 4.25 ± 0.74[2] | 0.34 | 18.45 | 100 | 0.390 ± 0.050 | 0.26 | 0.53 | 100 |
| ΣDDT | 19.17 ± 3.30[2] | 2.95 | 92.46 | 100 | 2.360 ± 0.185 | 1.84 | 2.89 | 100 |
| α-BHC | 0.02 ± 0.01 | 0 | 0.27 | 31.6 | 0.003 ± 0.002 | 0 | 0.01 | 33.6 |
| β-BHC | 0.53 ± 0.07[3] | 0.08 | 1.69 | 100 | 0.270 ± 0.100 | 0.11 | 0.75 | 100 |
| Lindane | 0.03 ± 0.01 | 0 | 0.29 | 55.3 | 0.008 ± 0.005 | 0 | 0.03 | 50.0 |
| Heptachlor epoxide | 0.08 ± 0.01 | 0.02 | 0.37 | 100 | 0.050 ± 0.010 | 0.01 | 0.08 | 100 |
| Oxychlordane | 0.13 ± 0.02[3] | 0.03 | 0.70 | 100 | 0.050 ± 0.020 | 0 | 0.12 | 67.6 |
| Dieldrin | 0.15 ± 0.02 | 0.04 | 0.62 | 100 | 0.120 ± 0.020 | 0.03 | 0.17 | 100 |
| % Fat | 3.75 | 1.63 | 10.10 | | 3.53 | 1.79 | 4.50 | |

[1] Means are ppm ± standard error of the mean, $N = 34$, high pesticide usage area; $N = 6$, low pesticide usage area.
[2] $P < 0.01$.
[3] $P < 0.05$.

TABLE 3. *Organochlorine pesticide residues in human milk, on a ppm whole milk basis, from women living in northwest and northeast Mississippi, 1973–75*

| Residue | High Pesticide Usage Area | | | Low Pesticide Usage Area | | |
|---|---|---|---|---|---|---|
| | Mean[1] | Min. | Max. | Mean[1] | Min. | Max |
| *p,p'*-DDE | 0.550 ± 0.130 | 0.056 | 3.946 | 0.067 ± 0.010 | 0.041 | 0.110 |
| *p,p'*-TDE | 0.002 ± 0.001 | 0 | 0.019 | < 0.001 | 0 | < 0.001 |
| *o,p'*-DDT | 0.008 ± 0.001 | 0 | 0.027 | 0.002 ± 0.001 | 0.001 | 0.005 |
| *p,p'*-DDT | 0.159 ± 0.030 | 0.010 | 0.810 | 0.014 ± 0.002 | 0.008 | 0.022 |
| ΣDDT | 0.719 ± 0.162 | 0.069 | 4.801 | 0.083 ± 0.012 | 0.051 | 0.130 |
| α-BHC | < 0.001 | 0 | 0.009 | < 0.001 | 0 | < 0.001 |
| β-BHC | 0.020 ± 0.004 | 0.002 | 0.105 | 0.009 ± 0.001 | 0.003 | 0.011 |
| Lindane | 0.001 ± 0.001 | 0 | 0.012 | < 0.001 | 0 | 0.001 |
| Heptachlor epoxide | 0.003 ± 0.001 | <0.001 | 0.020 | 0.002 ± <0.001 | <0.001 | 0.003 |
| Oxychlordane | 0.005 ± 0.001 | 0.001 | 0.022 | 0.002 ± 0.001 | 0 | 0.004 |
| Dieldrin | 0.006 ± 0.001 | 0.001 | 0.042 | 0.004 ± 0.001 | 0.001 | 0.007 |

[1] Means are ppm ± SEM; N = 34, high pesticide usage area; N = 6, low pesticide usage area.

from Australia are the only ones in the literature similar to those reported here.

Pesticide residues reported in Tables 2 and 3 indicate that women living in the Mississippi Delta, a high pesticide usage area, have one of the highest reported concentrations of ΣDDT residues in their milk. Although the appearance of pesticide residues in human tissues and milk is recognized as potentially hazardous, it is important to note that no adverse effects to infants due to this exposure have been documented.


### *Acknowledgment*

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# *Pesticide Residues in Human Milk, Alberta, Canada—1966–70, 1977–78*[1]

Robert A. Currie, V. William Kadis, Walter E. Breitkreitz,
George B. Cunningham,[2] and Gary W. Bruns

ABSTRACT

*Organochlorine pesticide residues were determined in human milk of residents of Alberta, Canada, during 1966–70 and 1977–78. Levels of polybrominated biphenyls (PBBs), polychlorinated biphenyls (PCBs), and some common organophosphorus pesticides were also monitored during 1977–78. Average residue levels were generally lower in 1977–78 samples, whereas the percent incidence of residues was generally lower in 1966–70 samples. β–BHC was found in all 1977–78 samples, but was not detected in 1966–70 samples. PCBs were detected in all but two of the 1977–78 samples. Average levels of p,p'-DDT and its metabolites were substantially lower during the second period than during the first. Large increases in the average levels and percent incidences of heptachlor epoxide and o,p'-DDT have been attributed to refinements in both cleanup and gas chromatographic analysis. Although no PBBs or organophosphorus pesticides were detected in 1977–78 samples, an unidentified hydrocarbon similar to dicofol was found in all samples of that period. No correlation between donor age groups and average pesticide residue levels could be inferred.*

## *Introduction*

Pesticide residues in human milk were first reported in 1951 by Laug et al. (*7*) who found DDT in 30 of their 32 samples. Since 1951, and particularly since the introduction of multiresidue screening by gas chromatography, numerous studies on levels of organochlorine pesticides and polychlorinated biphenyls (PCBs) in human milk have been reported throughout the world.

The present report describes two surveys of pesticide residue levels in human milk of residents of Alberta, Canada, during 1966–70 and 1977–78. The 1966–70 samples were analyzed only for residues of the common lipid-soluble organochlorine pesticides. During the second study, analysis included more organochlorine pesticides, some industrial chemicals, polybrominated biphenyls (PBBs) and PCBs, and the more common lipid-soluble organophosphorus pesticides.

## *Sampling and Analysis*

Human milk samples for the 1966–70 study were collected at the University of Alberta Hospital, Edmonton, Alberta, from women hospitalized for childbirth. The samples were obtained 2–10 days postpartum (mean, four days for the 53 donors who supplied this information) on a strictly voluntary basis, using a breast pump of unknown make. Samples were formalinized immediately after collection and stored upon receipt by the laboratory at −10°C until analysis. The majority of samples, 51 of 59, were from residents of the city of Edmonton; the balance came from residents of various parts of the Province of Alberta. The lipid content of the milk was 0.41–4.29 percent, based on 27 determinations, with a mean value of 1.86 percent. No correlation was evident between lipid percent and days postpartum. The maximum lipid value, 4.29 percent, was found in a sample obtained at three days postpartum. Information on racial origin of the donors or extraordinary exposure to pesticides was not available.

The lipid portion of the milk was extracted by the method of Kadis (*5*). Cleanup of an accurately weighed portion of the lipid material was performed on a Florisil column according to the method of Kadis et al. (*6*).

Residues were determined by electron-capture (tritium foil) gas chromatography of a 1.8 m × 3 mm OD borosilicate glass column packed with 25 percent DC–200/QF–1 (2:3) on 60–80-mesh Gas-Chrom Q. Results were confirmed on a gas chromatograph equipped with a Dohrmann microcoulometric detector in the halogen mode or by thin-layer chromatography using silica gel and $AgNO_3$ spray for detection. Although formalin used for initial preservation of the samples was not tested for possible interfering compounds, no problems were evident with the cleaned extracts at the gas chromatography stage.

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Samples for the second study were submitted to the laboratory by public health offices throughout the Province of Alberta between December 1977 and March 31, 1978, in direct response to a television program dealing with PCB and DDT residues in human milk. As in the first study, the majority of the samples, 24 of 33, originated in the city of Edmonton. Lipid content of samples was 0.27–5.45 percent on the basis of 24 determinations, with a mean value of 1.99 percent. Samples were collected 17–309 days postpartum (mean, 119 days); 27 of 33 donors made this information available. As in the first study, no correlation between milk lipid percent and days postpartum was evident. Residency information from 25 donors showed that 17 had been residents of the Province of Alberta longer than 5 years. Age was noted for 27 of 33 donors. No other epidemiological information was available. The samples were analyzed immediately upon receipt.

Lipids were extracted from the milk using Bureau of Dairy Industries (BDI) reagent described in *Standard Methods for the Examination of Dairy Products* (*1*). Volumetric flasks of suitable size were substituted for the test bottles, and the amounts of milk and reagent were scaled up proportionately. No solvents were added to the fat layer. The fat layer was drawn off with a disposable Pasteur pipet, dissolved in petroleum ether, and dried over anhydrous sodium sulfate. Following filtration and removal of the solvent, a weighed portion of the lipids, not exceeding 5 g, was partitioned four times between equal volumes of petroleum ether and acetonitrile to remove the bulk of the lipids. The acetonitrile extracts were partitioned back into petroleum ether, and the solvent was removed by drying over sodium sulfate. Samples were cleaned on Florisil and eluted in three fractions according to the method of Currie (*4*). For samples which yielded less than 1 g fat, the dried lipid material was diluted in 25 ml petroleum ether and applied directly to the Florisil column without acetonitrile partitioning.

Organohalogen residues were determined by electron-capture gas chromatography using modulated-pulse Ni–63 detectors. Fraction 1 from the Florisil column was examined for PBB residues on a 0.46 m × 6 mm OD borosilicate glass column packed with 6.8 percent DC–200/QF–1 (2:3) on 80–100-mesh Gas-Chrom Z at 240°C. This fraction was further examined for PCBs, ΣDDT, and other organochlorine pesticides known to elute in the fraction, on a 1 m × 6 mm OD borosilicate glass column packed with 12.5 percent OV–101/QF–1 (1:4) on 80–100-mesh Gas-Chrom Q. When PCBs were encountered, they were separated from other pesticides by the method of Snyder and Reinert (*9*).

Fraction 2 from the Florisil column was examined for organochlorine pesticides on a 1 m × 6 mm OD borosilicate glass column packed with 12.5 percent OV–101/QF–1 (2:3) on 80–100-mesh Gas-Chrom Q.

Fraction 3 from the Florisil column was examined for lipid-soluble organophosphorus pesticides by alkali-flame ionization detection on a 0.9 m × 6 mm OD borosilicate glass column packed with 5 percent QF–1 on 80–100-mesh Gas-Chrom Q.

Pesticides were partially confirmed by Florisil graded-elution described above. However, identities of pesticides in approximately every fourth sample were also confirmed by calculation of p-values (*2*).

Recoveries for the common lipid-soluble organochlorine and organophosphorus pesticides, PBBs, and PCBs exceeded 80 percent, except hexachlorobenzene (HCB). A 50 percent loss of HCB occurred during the acetonitrile-petroleum ether partitioning stage used to remove the bulk of the lipids from 1977–78 samples.

Quantitation was accomplished by the peak height comparison technique after adjusting pesticide concentrations in samples to values similar to those in the standards. Reliable quantitation limits were 0.001 ppm for the common lipid-soluble organochlorine pesticides, 0.01 ppm for PBBs and PCBs, and 0.02 ppm for common lipid-soluble organophosphorus pesticides. Organochlorine pesticides detected in 1966–70 samples included aldrin, α-BHC, *p,p′*-TDE, *p,p′*-DDE, *o,p′*-DDT, *p,p′*-DDT, dieldrin, endrin, heptachlor, heptachlor epoxide, and lindane. Samples from 1977–78 included the above compounds plus β-BHC, *cis*- and *trans*-chlordane, chlordene, *o,p′*-TDE, *o,p′*-DDE, HCB, kelthane, methoxychlor, mirex, PCNB, pentachlorobenzene (QCB), perthane, TCNB, and thiodan I. The following organophosphorus pesticides were sought in 1977–78 samples: ciodrin, diazinon, dursban, EPN, ethion, leptophos, leptophos phenol analog, malathion, methyl parathion, parathion, and phorate. Measured values of residues were not corrected for recoveries except values for HCB which were corrected to 100 percent.

## *Results and Discussion*

Mean pesticide levels, on an extractable lipid basis, found in all samples for both 1966–70 and 1977–78 surveys of human milk are given in Table 1. Trace quantities were arbitrarily assigned a value of zero for computational purposes. With a few exceptions, individual average residue levels are lower in the second survey than in the first, as is the total average pesticide residue load, i.e., the sum of the individual pesticides. However, in general, the incidence of pesticide residues increased during the time between the two surveys. The increase may, in part, be due to improvements in analytical technique. Although the primary result of these improvements has been greater assurance of pesticide identity, they could have played a small role in effecting generally lower residues in 1977–78. Differences in the sampling periods postpartum may also have influenced the generally lower residue levels in 1977–78. However,

TABLE 1. *Incidence and mean level of pesticide residues in extracted lipids of human milk samples, Alberta, Canada, 1966–70, 1977–78*

| Pesticide | Mean, ppm[1] | | Incidence, % | |
|---|---|---|---|---|
| | 1966–70 $N = 59$ | 1977–78 $N = 33$ | 1966–70 $N = 59$ | 1977–78 $N = 33$ |
| α-BHC | 0.107 | 0.002 | 37 | 76 |
| β-BHC | —[2] | 0.232 | —[2] | 100 |
| *p,p'*-TDE | 0.151 | 0.023 | 83 | 48 |
| *p,p'*-DDE | 2.23 | 1.09 | 100 | 100 |
| *o,p'*-DDT | 0.003 | 0.031 | 5 | 70 |
| *p,p'*-DDT | 1.14 | 0.437 | 97 | 100 |
| Dieldrin | 0.180 | 0.025 | 39 | 97 |
| Heptachlor epoxide | 0.002 | 0.028 | 5 | 94 |
| Hexachlorobenzene | —[2] | 0.091 | —[2] | 94 |
| PCBs | —[2] | 0.085 | —[2] | 100 |
| Lindane | 0.006 | ND | 3 | 0 |
| Unidentified hydrocarbon[3] | —[2] | 0.072 | —[2] | 100 |
| Total average pesticide load | 3.819 | 2.116 | — | — |

NOTE: ND = not detected.
[1] On extractable lipid basis.
[2] Not within the scope of the analytical procedure.
[3] Quantity estimated versus detector response for heptachlor epoxide.

Quinby et al. (*8*) found essentially no change in DDT and DDE levels in whole human milk sampled two to seven months postpartum from three individual donors. On the other hand, Curley and Kimborough (*3*) reported a 24 percent increase in the average ΣDDT in whole human milk sampled from five donors over 90–96 days postpartum.

No satisfactory explanation can be offered for the dramatic universal appearance of β-BHC in 1977–78. Although GC column analysis in the 1966–70 survey could not distinguish between lindane and β-BHC, lindane was found in only two of the 1966–70 samples, and the level in one of those was sufficiently high for its identity to be confirmed by thin-layer chromatography (TLC) using a silver nitrate reagent for detection.

As with lindane and β-BHC, the earlier GC column technology would not have allowed distinguishing between HCB and α-BHC except in certain cases. However, even if HCB was present in all the samples in which α-BHC was detected in the 1966–70 survey, it is obvious that the incidence of both HCB and α-BHC has more than doubled over the intervening years between the two surveys.

PCBs were detected in all but two of the 33 samples examined during the 1977–78 survey. However, during the earlier survey an awareness of the presence of PCBs and the methods for determining them were just being developed.

An unidentified hydrocarbon was found in all the second fractions from the graded-elution Florisil column used for cleanup of 1977–78 samples. At present the compound is thought to be structurally similar to dicofol which also elutes in fraction 2 of the Florisil column. The unknown has the same p-value as dicofol and the same retention time as dicofol on the 2:3 OV–101/QF–1 GC column. However, significant differences were observed between dicofol and the unknown on TLC and in their retention times on a 1:4 OV–101/QF–1 GC column. Although the unknown was not reported during the 1966–70 survey, its presence cannot be precluded because the single-fraction elution system used during the early survey may have allowed it to be masked by other residues. An attempt will be made to identify the unknown by means of GC-mass spectrometry.

The large increases in the average levels and the percent incidences of heptachlor epoxide and *o,p'*-DDT are perhaps the most striking results of the two surveys. Use of DDT and heptachlor epoxide had been greatly curtailed during the years between the two surveys, and one would normally have expected both the percent incidences and the average levels to have followed a pattern similar to that of dieldrin. The usage pattern of dieldrin closely approximated that of heptachlor epoxide during these years, and although dieldrin's percent incidence is up, its average level is substantially lower as one might expect. Also, the average levels of *p,p'*-DDT and its metabolites are substantially lower in the second survey than in the first survey. At the present time, the most satisfactory explanation for these apparent anomalies is the improvement and refinement in cleanup and GC column technology.

The ranges of pesticides found in both surveys, and their percent incidences, are given in Table 2. Com-

TABLE 2. *Incidence and range of pesticide residues in extracted lipids of human milk samples, Alberta, Canada, 1966–70, 1977–78*

| Pesticide | Range, ppm[1] | | Incidence, % | |
|---|---|---|---|---|
| | 1966–70 | 1977–78 | 1966–70 $N = 59$ | 1977–78 $N = 33$ |
| α-BHC | ND–0.733 | ND–0.016 | 37 | 76 |
| β-BHC | —[2] | 0.009–0.393 | —[2] | 100 |
| *p,p'*-TDE | ND–1.45 | ND–0.348 | 83 | 48 |
| *p,p'*-DDE | 0.173–8.12 | 0.258–5.18 | 100 | 100 |
| *o,p'*-DDT | ND–0.072 | ND–0.169 | 5 | 70 |
| *p,p'*-DDT | ND–11.25 | TR–8.35 | 97 | 100 |
| Dieldrin | ND–4.66 | ND–0.081 | 39 | 97 |
| Heptachlor epoxide | ND–0.060 | ND–0.113 | 5 | 94 |
| Hexachlorobenzene | —[2] | TR–5.13 | —[2] | 94 |
| Lindane | ND–0.340 | ND | 3 | 0 |
| PCBs | —[2] | ND–0.751 | —[2] | 100 |
| Unidentified hydrocarbon[3] | —[2] | 0.014–0.258 | —[2] | 100 |
| Maximum range | ND–11.25 | ND–8.35 | — | — |

NOTE: ND = Not detected; TR = trace.
[1] On extractable lipid basis.
[2] Not within scope of the analytical procedure.
[3] Quantity estimated versus detector response for heptachlor epoxide.

TABLE 3. *Distribution of mean pesticide residue level in extracted lipids of human milk according to age of donor, Alberta, Canada, 1966–70*

| Age Group | <21 | 21–25 | 26–30 | 31–35 | >35 |
|---|---|---|---|---|---|
| No. of Donors | 4 | 18 | 21 | 10 | 6 |
| Pesticide | Mean, ppm[1] | | | | |
| α-BHC | 0.195 | 0.135 | 0.075 | 0.087 | 0.114 |
| *p,p'*-TDE | 0.189 | 0.129 | 0.197 | 0.101 | 0.114 |
| *p,p'*-DDE | 2.31 | 2.13 | 2.24 | 2.12 | 2.64 |
| *o,p'*-DDT | ND | ND | 0.008 | ND | ND |
| *p,p'*-DDT | 1.34 | 0.866 | 1.29 | 0.973 | 1.46 |
| Dieldrin | 0.089 | 0.066 | 0.174 | 0.049 | 0.81 |
| Heptachlor epoxide | ND | ND | 0.033 | ND | 0.016 |
| Lindane | ND | ND | 0.010 | 0.034 | ND |
| Total average load | 4.123 | 3.326 | 4.027 | 3.364 | 5.154 |

NOTE: ND = not detected.
[1] On extractable lipid basis.

TABLE 4. *Distribution of mean pesticide residue levels in extracted lipids of human milk according to age of donor, Alberta, Canada, 1977–78*

| Age Group | <21 | 21–25 | 26–30 | 31–35 | Unknown |
|---|---|---|---|---|---|
| No. of Donors | 1 | 10 | 11 | 5 | 6 |
| Pesticide | Mean, ppm[1] | | | | |
| α-BHC | 0.001 | 0.003 | 0.002 | 0.002 | 0.003 |
| β-BHC | 0.014 | 0.072 | 0.536 | 0.094 | 0.092 |
| *p,p'*-TDE | ND | 0.028 | 0.012 | 0.070 | ND |
| *p,p'*-DDE | 0.699 | 1.10 | 1.01 | 1.41 | 1.03 |
| *o,p'*-DDT | ND | 0.016 | 0.042 | 0.066 | 0.014 |
| *p,p'*-DDT | TR | 0.134 | 0.218 | 0.275 | 1.55 |
| Dieldrin | 0.015 | 0.018 | 0.032 | 0.030 | 0.023 |
| Heptachlor epoxide | 0.016 | 0.015 | 0.040 | 0.025 | 0.030 |
| Hexachlorobenzene | 0.009 | 0.057 | 0.110 | 0.107 | 0.081 |
| PCB | ND | 0.044 | 0.052 | 0.250 | 0.121 |
| Unidentified hydrocarbon | 0.065 | 0.061 | 0.056 | 0.082 | 0.109 |
| Total average load | 0.819 | 1.548 | 2.111 | 2.411 | 3.053 |

NOTE: ND = not detected; TR = trace.
[1] On extractable lipid basis.

ments made regarding average levels of pesticides also apply to the ranges of levels.

Samples collected for the second survey were also analyzed for PBBs and the common lipid-soluble organophosphorus pesticides, but none was detected.

The distribution of mean pesticide residue levels in the extracted lipids of human milk for both the 1966–70 and 1977–78 surveys are shown in Tables 3 and 4, respectively, according to age of donor. No correlation between donor age groups and average pesticide residue levels could be inferred. It is possible, however, that other factors such as the number of previous children the donor had nursed and the donor's dietary habits may have a greater influence on pesticide residue levels than does age alone.

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# FISH, WILDLIFE, AND ESTUARIES

## *Organochlorine Residues in Six Species of Estuarine Birds, South Carolina, 1971–75*

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ABSTRACT

*In South Carolina between 1971 and 1975, authors evaluated the occurrence of organochlorine residues in the laughing gull* (Larus atricilla), *white ibis* (Eudocimus albus), *glossy ibis* (Plegadis falcinellus), *American oystercatcher* (Haematopus palliatus), *willet* (Catoptrophorus semipalmatus), *and ruddy turnstone* (Arenaria interpres). *Tissues of birds found dead and eggs were analyzed, eggshell thicknesses were measured, and incidental observations were made of reproductive success and population status. Eggshell thicknesses of the white ibis, American oystercatcher, and laughing gull were not significantly different* ($P < 0.05$) *from the pre-1947 norms. DDE and polychlorinated biphenyls (PCBs) were found most frequently and at the highest concentrations in eggs. DDE residues declined significantly in oystercatcher eggs, and declined slightly in laughing gull eggs; no change was noted in white ibis eggs. No consistent trends were found for dieldrin and PCBs. Authors found no obvious problems with reproductive success of any species. Populations of the five species breeding in South Carolina appear stable. The white ibis and laughing gull in South Carolina have experienced population explosions over the past 50 years; the glossy ibis has increased substantially since the first documented breeding records in 1947.*

### *Introduction*

Authors' studies of the effects of pollutants on estuarine birds in the southeastern United States have focused on the brown pelican (*Pelecanus occidentalis*), a sensitive indicator species for certain organochlorine pollutants (*1, 3*). However, studies in South Carolina included other estuarine birds which appeared to be less sensitive to organochlorines than is the pelican (*6*). Six of the species included the laughing gull (*Larus atricilla*), white ibis (*Eudocimus albus*), glossy ibis (*Plegadis falcinellus*), American oystercatcher (*Haematopus palliatus*), willet (*Catoptrophorus semipalmatus*), and ruddy turnstone (*Arenaria interpres*). The purposes of the present study were to analyze eggs and tissues for organochlorine residues, to measure eggshell thicknesses, and to obtain incidental information on breeding biology and population status of several of the species.

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### *Procedure for Sampling, Necropsy, and Field Study*

From 1971 to 1975 authors visited islands in South Carolina estuaries during the breeding season to collect eggs and dead birds and to record incidental information on breeding biology and population status. Most of the research was conducted on or near the Cape Romain National Wildlife Refuge (CRNWR).

Addled and viable eggs in all stages of incubation were collected. One egg was usually taken from each nest selected for sampling. Eggs were weighed and measured. Their contents were removed and placed in chemically cleaned glass bottles that had been rinsed with acetone, hexane, deionized water, and dilute nitric acid; filled bottles were placed in a freezer. Eggshells were thoroughly rinsed with tap water and were allowed to dry. Shell thickness, shell plus shell membranes, was measured at three sites on the waist of the egg with a micrometer graduated in units of 0.01 mm.

Two oystercatchers found dead were collected and frozen. The specimens were removed from the freezer several months later, allowed to thaw, and subsequently necropsied. Tissues for histological study were fixed in 10 percent formalin, embedded in paraffin, sectioned, and stained (*15*). The entire brain was removed and placed in a chemically cleaned glass bottle. The remaining carcasses, except for skin, feet, wings, liver, kidney, and gastrointestinal tract, were wrapped in foil and refrozen. The brains and carcasses were later analyzed for organochlorine residues.

### *Analytical Procedures*

Contents of each egg collected in 1971 were homogenized, and a 20-g portion was mixed with anhydrous sodium sulfate in a blender and extracted for 7 hours with hexane in a Soxhlet apparatus. The extract was

TABLE 1. *Eggshell thickness of four species of estuarine birds, South Carolina, 1947–75*

| Species | Eggshell Thickness, mm [1] | | | | |
|---|---|---|---|---|---|
| | Pre-1947 | 1971 | 1972 | 1974 | 1975 |
| White ibis | 0.334[2]± 0.005 (27) | | 0.335± 0.011 (10) | 0.335± 0.005 (10) | |
| American oystercatcher | 0.308± 0.001 (192) | 0.290± 0.013 (5) | 0.313± 0.006 (11) | | 0.303± 0.005 (13) |
| Laughing gull | 0.280± 0.007 (4) | 0.271± 0.003 (15) | | | 0.268± 0.007 (11) |
| Glossy ibis | | | 0.290± 0.008 (10) | | |

[1] Mean ± standard error; sample size in parentheses.
[2] Thickness means were not significantly different ($P > 0.05$). Means were separated by multiple range tests (*11, 13*).

cleaned by acetonitrile partitioning and was eluted on partially deactivated Florisil. For pesticide analysis, residues in the cleaned extract were separated and removed in four fractions from a silica gel thin-layer plate (*15*). Each thin-layer fraction was analyzed by electron-capture gas chromatography (GC) on a column of 3 percent OV-1 or 3.8 percent UCW-98 on Chromosorb W(HP). DDT and its metabolites in fractions III or IV were confirmed on a column of 3 percent XE-60 or 3 percent QF-1 on Gas-Chrom Q. Polychlorinated biphenyls (PCBs) were identified and measured semiquantitatively by thin-layer chromatography (*14*).

For eggs collected between 1972 and 1975, the methodology was modified as described by Cromartie et al. (*9*). The extract of the 10-g portion was cleaned on a Florisil column. Pesticides and PCBs were separated into three fractions on a SilicAR column and analyzed by GC on a 4 percent SE-30/6 percent QF-1 column. By this method, authors could detect additional pesticides, including toxaphene, *cis*-chlordane or *trans*-nonachlor, and *cis*-nonachlor. In 1972, there was no standard for quantitating *cis*-nonachlor and in 1973, a procedure was first developed to estimate toxaphene levels. For the eggs collected during 1974–75, the lipids were removed either on a Florisil column or by automated gel permeation chromatography. In 1974, authors separated and quantitated *cis*-chlordane and *trans*-nonachlor on a 1.5 percent OV-17/1.95 percent QF-1 column.

Residues in 10 percent of the samples were confirmed by GC-mass spectrometry. Average recoveries from spiked samples were 75–112 percent. Residues were not corrected for recovery. Weights of egg contents were corrected for moisture loss by use of egg volume (*21*); residues are expressed as fresh wet weight.

## Results

### EGGSHELL THICKNESS

Eggshells of the white ibis, American oystercatcher, laughing gull, and glossy ibis were measured for thickness (Table 1). No pre-1947 thickness data for the glossy ibis from South Carolina were available, and only a small sample was located for the laughing gull. Eggshell thickness means of eggs collected during the 1970s were not significantly different ($P > 0.05$; range, −4.3 to +1.6 percent) from pre-1947 norms (Table 1). In Texas, eggshell thinning averaged <4 percent for the laughing gull and white ibis in 1970 (*12*). In the present study, authors did not observe any obviously thin-shelled, cracked, or crushed eggs.

### ORGANOCHLORINE RESIDUES

Residues of 10 organochlorines were found in 84 eggs of four species (Tables 2–5). DDE and PCBs were detected most frequently and at the highest levels; DDE was detected in all eggs, PCBs in 68 percent, and dieldrin in 33 percent. Residues in laughing gull (Table 4) and glossy ibis (Table 5) eggs were slightly higher than residues in eggs of the oystercatcher (Table 2) or white ibis (Table 3). The highest residues found in individual

TABLE 2. *Residues of organochlorines in eggs of the American oystercatcher, South Carolina, 1971–75*

| Year | Residues, µg/g Fresh Wet Weight | |
|---|---|---|
| | DDE | PCBs |
| 1971 | 1.10 | — |
| | 0.96[1] | — |
| | 1.10[2] | — |
| | 0.74 | — |
| | 0.77 | — |
| Geometric mean | 0.92 | — |
| 95% Confidence limits | 0.73–1.17 | — |
| Range | 0.74–1.10 | ND |
| 1972 | 0.44 | 1.0 |
| | 0.54 | 0.9 |
| | 0.71 | — |
| | 0.30 | 0.9 |
| | 0.38 | 1.0 |
| | 0.40 | 1.0 |
| | 0.74 | 0.9 |
| | 0.41 | 0.8 |
| | 0.45 | 0.9 |
| | 0.42 | 0.8 |
| Geometric mean | 0.46 | 0.8 |
| 95% Confidence limits | 0.39–0.56 | 0.6–1.1 |
| Range | 0.30–0.74 | ND–1.0 |
| 1975 | 0.28 | 0.5 |
| | 0.25 | 0.5 |
| | 0.24 | 0.6 |
| | 0.25[3] | 0.5 |
| | 0.20 | — |
| | 0.25 | 0.5 |
| | 0.45 | 0.7 |
| | 0.33 | 0.5 |
| | 0.21 | — |
| | 0.33 | 0.5 |
| | 0.24 | 0.5 |
| | 0.25 | 0.5 |
| | 0.15 | 0.5 |
| Geometric mean | 0.26 | 0.5 |
| 95% Confidence limits | 0.22–0.30 | 0.4–0.6 |
| Range | 0.15–0.45 | ND–0.7 |

[1] 0.12 µg/g of dieldrin.
[2] 0.13 µg/g of dieldrin.
[3] 0.63 µg/g of toxaphene.

TABLE 3. *Residues of organochlorine pollutants in eggs of the white ibis, South Carolina, 1972, 1974*

| Year | Residues, µg/g Fresh Wet Weight | | | |
|---|---|---|---|---|
| | DDE | Dieldrin | Mirex | PCBs |
| 1972 | 0.19 | — | 0.12 | — |
| | 0.68 | 0.10 | — | 1.2 |
| | 1.02 | — | 0.21 | 0.6 |
| | 0.45 | — | 0.20 | — |
| | 1.27[1] | — | 0.13 | — |
| | 0.20 | — | — | — |
| | 0.42 | — | — | 1.1 |
| | 1.46[2] | — | — | 0.8 |
| | 0.32 | — | 0.39 | — |
| | 0.19 | — | — | — |
| Geometric mean | 0.48 | — | — | — |
| 95% Confidence limits | 0.27–0.83 | — | — | — |
| Range | 0.19–1.46 | ND–0.10 | ND–0.39 | ND–1.2 |
| 1974 | 0.88 | 0.10 | — | 1.8 |
| | 0.85 | 0.11 | — | 1.0 |
| | 0.35 | — | — | 0.5 |
| | 0.43 | — | — | — |
| | 0.14 | — | — | — |
| | 0.68 | — | — | 0.5 |
| | 0.53 | — | — | — |
| | 0.43 | — | — | 0.5 |
| | 0.83 | — | — | — |
| | 0.65[3] | — | — | 0.5 |
| Geometric mean | 0.52 | — | — | 0.6 |
| 95% Confidence limits | 0.35–0.77 | — | — | 0.4–0.8 |
| Range | 0.14–0.88 | ND–0.11 | ND | ND–1.8 |

[1] 0.10 µg/g of DDT.
[2] 0.18 µg/g of DDT.
[3] 0.28 µg/g of *trans*-nonachlor.

TABLE 4. *Residues of organochlorine pollutants in eggs of the laughing gull, South Carolina, 1971, 1975*

| Year | Residues, µg/g Fresh Wet Weight | | |
|---|---|---|---|
| | DDE | Dieldrin | PCBs |
| 1971 | 1.55 | — | — |
| | 1.81 | 0.14 | 4.8 |
| | 2.08 | 0.24 | 2.0 |
| | 0.70 | — | — |
| | 1.04 | 0.14 | 5.9 |
| | 1.05 | 0.12 | 2.4 |
| | 1.54 | 1.83 | 2.7 |
| | 1.29 | 0.14 | 2.1 |
| | 0.55 | 0.24 | 6.3 |
| | 3.33 | 0.18 | 9.5 |
| | 2.25[1] | 0.17 | 3.9 |
| | 2.57 | 0.29 | 4.7 |
| | 1.18 | 0.10 | 1.0 |
| | 1.46 | 0.19 | 1.9 |
| | 1.09 | — | 3.4 |
| Geometric mean | 1.41 | 0.16 | 2.6 |
| 95% Confidence limits | 1.08–1.84 | 0.11–0.25 | 1.6–4.2 |
| Range | 0.55–2.57 | ND–1.83 | ND–9.5 |
| 1975 | 2.00 | 0.11 | 2.2 |
| | 1.10 | 0.25 | 4.8 |
| | 0.65 | — | 1.9 |
| | 0.85 | — | 2.1 |
| | 1.30 | — | 1.5 |
| | 0.65 | — | 1.0 |
| | 1.20 | 0.17 | 1.2 |
| | 1.40[2] | 0.22 | 1.7 |
| | 2.20[3] | 1.50 | 4.3 |
| | 0.83 | 0.23 | — |
| | 1.40 | 0.14 | 2.8 |
| Geometric mean | 1.14 | 0.14 | 1.6 |
| 95% Confidence limits | 0.87–1.50 | 0.07–0.27 | 1.1–2.4 |
| Range | 0.65–2.20 | ND–1.50 | ND–4.8 |

[1] 0.29 µg/g of mirex.
[2] 0.10 µg/g of toxaphene.
[3] 0.18 µg/g of heptachlor epoxide, 0.18 µg/g of oxychlordane, 0.12 µg/g of *cis*-chlordane, 0.19 µg/g of *trans*-nonachlor, and 0.11 µg/g of toxaphene.

TABLE 5. *Residues of organochlorines in eggs of the glossy ibis, South Carolina, 1972*

| Year | Residues, µg/g Fresh Wet Weight | | | |
|---|---|---|---|---|
| | DDE | DDT | Dieldrin | PCBs |
| 1972 | 2.26 | 0.19 | 1.72 | 0.6 |
| | 1.12 | — | — | — |
| | 0.27 | — | — | — |
| | 1.57 | — | 0.15 | — |
| | 0.94 | 0.17 | — | — |
| | 7.70[1] | 0.21 | 0.33 | 0.5 |
| | 3.44[2] | 2.64 | 2.16 | — |
| | 1.28 | — | — | 0.6 |
| | 4.54 | 0.14 | — | — |
| | 0.34 | — | — | — |
| Geometric mean | 1.49 | | | |
| 95% Confidence limits | 0.69–3.19 | | | |
| Range | 0.27–7.70 | ND–2.64 | ND–2.16 | ND–0.6 |

[1] 0.12 µg/g of mirex.
[2] 0.72 µg/g of TDE.

eggs were: 7.70 µg/g DDE, glossy ibis; 2.16 µg/g dieldrin, glossy ibis; and 9.5 µg/g PCBs, laughing gull. DDE residues declined significantly in oystercatcher eggs (Table 2), declined slightly in laughing gull eggs (Table 4), and were unchanged in white ibis eggs (Table 3). There were no consistent trends for dieldrin and PCBs.

DDE and PCBs were the only residues detected in brains and carcasses of seven birds found dead in South Carolina (Table 6). Residues were generally very low. DDE and PCBs were detected in three of seven brains. Only two oystercatchers were necropsied; one died of avian cholera (*2*) and the other of nephrosis (Table 6).

### BREEDING SITES AND POPULATION STATUS

Except for the ruddy turnstone, all of the species breed in South Carolina. Authors found the willet, a solitary nester that builds a well concealed nest, nesting on Bird Key (Stono River), Deveaux Bank, and on islands on the CRNWR including Cape Island, Raccoon Key, Bird Bank, and Marsh Island. Authors observed only one young willet. Population status of the species is indefinite; the willet is widespread on the coastal islands, but is not numerous in any area.

The oystercatcher is essentially a solitary nester, although nests may be found close together at times. Unlike willet eggs, oystercatcher eggs are laid in a small cavity or scrape that the birds dig in sand or shells and, with few exceptions, the scrapes are dug in sites with no vegetative cover. Authors found oystercatcher nests on a number of coastal islands and on the spoil deposited along the banks of the Intracoastal Waterway in South Carolina. The oystercatcher population is apparently in good condition, although quantitative data to establish trends are unavailable.

The glossy ibis was first found nesting in South Carolina in 1947 (*18*), and the population had increased to about 700 pairs by 1975 (*10*). Nesting sites ranged from barrier islands with small shrubs, specifically, Marsh

TABLE 6. *Residues of organochlorines in tissues of three species of estuarine birds, South Carolina, 1971–74*

| Species | Year | Age | Sex | Residues, µg/g Fresh Wet Weight | | | Cause of Death |
|---|---|---|---|---|---|---|---|
| | | | | Tissue | DDE | PCBs | |
| Ruddy turnstone | 1974 | Ad | Unk | Brain | 0.27 | 3.0 | Open |
| | | Ad | Unk | Brain | — | 3.4 | Open |
| | | Ad | Unk | Brain | — | 7.0 | Open |
| Willet | 1973 | Ad | Unk | Brain | 0.20 | — | Open |
| American oystercatcher | 1971 | Ad | F | Brain | 0.10 | — | Nephrosis |
| | | | | Carcass | 0.40 | — | |
| | 1973 | Ad | Unk | Brain | — | — | Open |
| | | Ad | F | Brain | — | — | Avian cholera |
| | | | | Carcass | 0.45 | — | |

NOTE: Open = unknown at this time.

Island and White Banks on the CRNWR and Deveaux Bank, to a large wooded island, Drum Island, in the Cooper River at Charleston.

Authors found white ibis nesting in three colonies in 1975; inactive nests from the previous year were observed in another colony on Hilton Head Island. Since 1922 when the species was first found nesting in South Carolina (*19*), the population had increased to about 31,000 breeding pairs by 1975. The colony on Pumpkinseed Island near Georgetown contained 19,000 pairs and the Drum Island colony consisted of 12,000 pairs; only two pairs were located in an inland swamp colony near Conway (*10*).

History of the laughing gull in South Carolina is similar to that of the white ibis. There is only one nesting record for this species before 1933, although adults were seen in previous years in South Carolina estuaries throughout the usual breeding season (*20*). Since the recorded nesting in South Carolina in 1933 (*7*), the gulls have undergone a population explosion. Rough estimates in 1975 indicated more than 10,000 breeding pairs in the state. Laughing gulls nest on almost all of the South Carolina barrier islands.

General observations indicated that the laughing gull, white ibis, and glossy ibis experienced excellent reproductive success. There were insufficient observations to estimate reproductive success in the oystercatcher and willet, but there were no obvious problems.

## *Discussion*

Low organochlorine residues in the oystercatcher probably reflect low residues in the oyster (*Crassostrea virginica*), another shellfish consumed by this species. Residues in oysters in South Carolina were declining in the late 1960s. So few oysters contained detectable levels of organochlorine pesticides in 1969 that monitoring was discontinued (*8*). The decline in DDE residues in oystercatcher eggs from 1971 to 1975 apparently reflects a further decline in residues in food of the oystercatcher. Authors have noted significant declines of DDE in eggs of other birds from South Carolina estuaries including the brown pelican (*4*) and the least tern (*Sterna albifrons*) (*5*) which parallel decreases of organochlorine pollutants in certain estuarine fish.

The low mean residues found in eggs of the white ibis and laughing gull from South Carolina differed from means in the same species from other areas. Laughing gull eggs collected in Texas in 1970 (*12*) contained more DDE ($\sim 10$ µg/g), dieldrin (0.52 µg/g), and PCBs (3.00 µg/g) than did South Carolina eggs. White ibis eggs collected in Texas in 1970 (*12*) and in the southeastern United States in 1972–73 (*17*) contained lower DDE ($< 0.4$ µg/g) and PCB ($< 0.2$ µg/g) residues than did South Carolina eggs.

Laughing gulls are most numerous on islands such as Bird Bank, Marsh Island, and Deveaux Bank where royal terns (*Sterna maxima*) and Sandwich terns (*Sterna sandvicensis*) nest. Gulls catch live fish and other prey animals, but they also obtain food regurgitated by terns, particularly by chicks. Large numbers of tern eggs that are washed out of nests by tidewaters can be a substantial food source for the gulls. Laughing gulls seldom preyed on royal and Sandwich tern eggs; however, laughing gull depredation of eggs of the black skimmer (*Rynchops niger*) and gullbilled tern (*Gelochelidon nilotica*) was apparently the major factor in reproductive failure of those species on Deveaux Bank from 1972 to 1975.

Laughing gulls, together with royal and Sandwich terns, deserted Marsh Island in 1976 and nested on Bird Bank. On June 16, 1973, a partial count revealed 629 laughing gull nests on several of the small islands known collectively as White Banks (CRNWR); the actual number was probably near 1000 nests. Royal and Sandwich terns did not nest at White Banks during the present study. The laughing gulls nesting on White Banks seemed to feed extensively on shrimp heads, waste fish, pieces of crab, and other materials originating from shrimp trawlers on nearby Five Fathom Creek, from a nearby crab processing plant, and from other commercial fishing activities.

The low organochlorine residues in eggs and tissues of the birds apparently exerted negligible effects on eggshell thickness, reproductive success, and adult survival.

Populations of the five species breeding in South Carolina appear stable. Alterations of the estuarine environment through dredging, commercial fishing, or other activities may have created conditions that favored population increases in the glossy ibis, white ibis, and laughing gull. The increases in the glossy ibis and white ibis populations may be related to a general northward expansion of the breeding range in combination with continued recovery of populations decimated by human disturbance early in this century (*16*). Authors feel that this explanation may suffice for the population increase of glossy ibis; however, the increase in white ibis seems related primarily to changes in the habitat, particularly creation of dredge islands for nesting. The population dynamics of the laughing gull seem distinct from the other two species in that there has been no general latitudinal expansion in the Atlantic coast population. Thus, at this point, we have little real insight into the mechanisms underlying fluctuations in populations of the three species in South Carolina.


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# *Shell Thinning and Residues of Organochlorines and Mercury in Seabird Eggs, Eastern Canada, 1970–76*

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## ABSTRACT

*Organochlorine and mercury concentrations are reported for 252 eggs of Leach's storm-petrel* (Oceanodroma leucorhoa), *double-crested cormorant* (Phalacrocorax auritus), *common eider* (Somateria mollissima), *common tern* (Sterna hirundo), *razorbill* (Alca torda), *common murre* (Uria aalge), *black guillemot* (Cepphus grylle), *and Atlantic puffin* (Fratercula arctica) *from the Bay of Fundy, the Gulf of St. Lawrence, and the open Atlantic shore of Canada during 1970–76. Concentrations of all organochlorines except DDE and polychlorinated biphenyls (PCBs) were low. DDE, PCBs, and mercury residues were highest in cormorant and petrel, intermediate in alcids, and lowest in eider and tern. Temporal and spatial aspects of contamination patterns are discussed. Authors conclude that only in cormorants were DDE residues high enough to cause, through eggshell thinning, local population declines.*


## *Introduction*

During the past century marked changes have occurred in some seabird populations of the western Atlantic (*19*). Leach's storm-petrel (*Oceanodroma leucorhoa*) has decreased in the Bay of Fundy, the Gulf of Maine, and the Gulf of St. Lawrence. Populations of double-crested cormorant (*Phalacrocorax auritus*) have increased considerably since the turn of the century, apparently due to decreased human predation; however, recent declines have occurred in the Gulf of St. Lawrence. Terns have declined on the North American Atlantic seaboard although three species of gulls have increased. Alcid populations generally have declined; decreases of the razorbill (*Alca torda*) in the Gulf of St. Lawrence have been particularly marked.

Few chemical pollutant residue data have been published for seabirds off the northeastern coast of North America. Organochlorine concentrations in petrels and alcids in Newfoundland, and in marine double-crested cormorants in the Gulf of Maine-Bay of Fundy region have been reported (*14, 16, 35*). Major sources of pollutant contamination of the Gulf of St. Lawrence have been discussed (*33*). DDE contamination of that basin in the late 1960s was thought to be high enough to have contributed to low productivity of gannets (*Morus bassanus*) (*18*). PCB and DDE concentrations in the eggs of seabirds of western Canadian coastal waters were given in a review of the exposure of marine birds to environmental pollutants (*20*). In the present paper authors present organochlorine and mercury residue concentrations found in seabird eggs collected on the Canadian Atlantic seaboard during 1970–76, and attempt to assess the implications of the contamination on the productivity of the birds.

## *Sampling, Materials, and Methods*

Eggs of Leach's storm-petrel, double-crested cormorant, common eider (*Somateria mollissima*), common tern (*Sterna hirundo*), razorbill, common murre (*Uria aalge*), black guillemot (*Cepphus grylle*), and Atlantic puffin (*Fratercula arctica*) were collected from various sites in eastern Canada (Fig. 1) between 1970 and 1976. At most sites, eggs were taken early in the nesting season. Eggs were taken from first clutches at cormorant and tern colonies because the species re-lay if the first clutch is destroyed. One egg was taken from each of five or ten nests near the center of the colony. The maximum length and width of each egg was measured and, after the contents had been removed, the eggshell was washed, dried, and weighed. Eggshell thickness indices, weight(mg)/length(mm) $\times$ width(mm), were calculated. Pending analysis, egg contents were stored frozen.

## *Analytical Procedures*

### ORGANOCHLORINES

The frozen egg sample was thawed, and homogenized in a Waring Blendor. A 2–5-g aliquot of the blend was weighed to the nearest milligram and was oven-dried for about 24 hours at 45°C with slight vacuum (water aspirator) to constant weight. The dried sample was ground with 5–10 g anhydrous sodium sulfate. The


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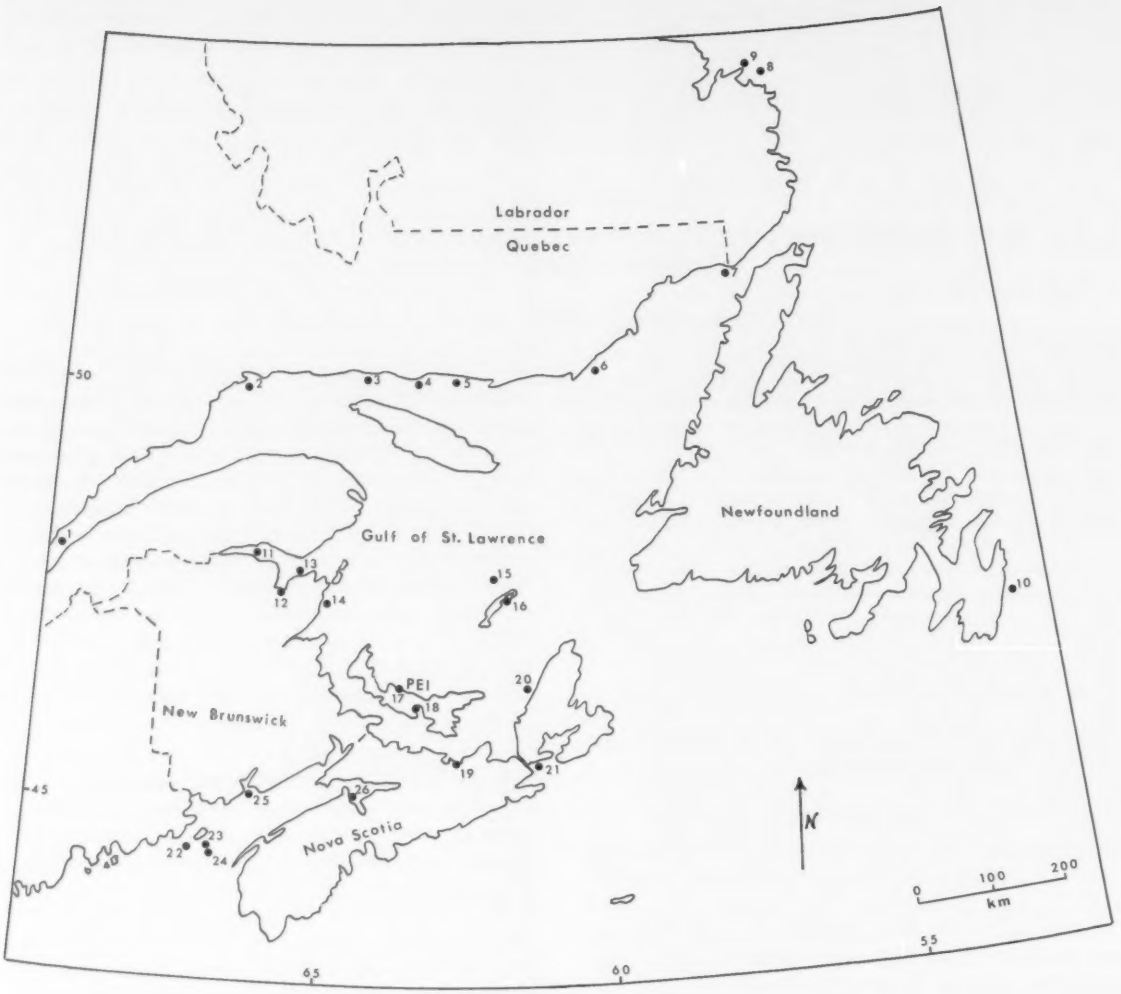


FIGURE 1. *Locations of seabird egg-sampling sites in the Atlantic Provinces and eastern Quebec, 1970–76*

1. Ile-aux-Pommes, Quebec.
2. Carrousel Island, Quebec.
3. Inner Birch Island, Quebec.
4. Betchouane, Quebec.
5. Watshishu, Quebec.
6. Ile Ste-Marie, Quebec.
7. Perroquet Island, Quebec.
8. Gannet Island, Newfoundland.
9. Bird Island, Newfoundland.
10. Great Island, Newfoundland.
11. Heron Island, New Brunswick.
12. Bathurst, New Brunswick.
13. Riorden, New Brunswick.
14. Tabusintac, New Brunswick.
15. Brion Island, Quebec.
16. Magdalen Islands, Quebec.
17. Cape Tryon, Prince Edward Island.
18. Charlottetown, Prince Edward Island.
19. Pictou, Nova Scotia.
20. Margaree Island, Nova Scotia.
21. Campbell Island, Nova Scotia.
22. Machias Seal Island, New Brunswick.
23. Low Duck Island, New Brunswick.
24. Kent Island, New Brunswick.
25. Manawagonish Island, New Brunswick.
26. Boot Island, Nova Scotia.

sample was extracted in a Soxhlet apparatus for 2 hours with 150 ml of a 1:3 mixture of ether-hexane at a rate of 10 siphonings/hour. After extraction, the solvent was removed in a Rotovapor flash evaporator, the dried flask was weighed, and the percent fat was calculated.

Some minor modifications were made during the investigation. For eggs collected during 1970–71, cleanup involved the cold precipitation of fats with filtration through a carbon-Celite pad at —70°C (*34*). Prior to the present study, the authors became aware of the presence of PCBs in other wildlife samples, and there-

fore developed a Florisil separation method (*28*). Thus all organochlorine residue data reported here are free of PCB interference. PCB estimations were made with Aroclor 1260 as the reference standard, and are the averages of calculations for peaks No. 8 and No. 10. In the cleanup of extracts of samples collected during 1972–73, an alumina-Celite pad was substituted for the carbon-Celite pad used in the cold filtration process to improve PCB recoveries (*7*). Cleanup procedures for the 1974–76 specimens were based on the use of 2 percent water-deactivated Florisil (*29*).

A chromatographic glass column was packed with 15 cm of regular grade Florisil which had been heated to 300°C and then deactivated with 2 percent water. The Florisil was topped with 1 cm sodium sulfate and the column was washed with 100 ml hexane. A maximum of 0.5 g oil or fat from the sample extract was mixed with approximately 5 ml hexane and placed in the column. Two fractions were eluted successively at approximately 5 ml/minute as follows: Fraction I, eluted with 130–135 ml hexane, contained DDE, hexachlorobenzene (HCB), and PCBs; Fraction II, eluted with 300 ml of 30 percent dichloromethane in hexane, contained TDE, DDT, dieldrin, endrin, and heptachlor epoxide.

Analyses were performed on a Hewlett-Packard Model 5700 gas chromatograph equipped with linear $Ni^{63}$ electron-capture detector, a Model 7671A automatic sample injector, and a Model 7123A recorder. Instrument parameters and operating conditions follow:

| | |
|---|---|
| Column: | 0.64 cm × 183 cm × 4 mm ID, glass spiral, packed with a mixture of 3 percent OV-101 and 5 percent OV-210 on 80–100-mesh Chromosorb W (HP) |
| Temperatures: | injector 215°C<br>detector 300°C<br>column 215°C |
| Carrier gas: | 5 percent methane in argon flowing at 60 ml/minute |

The sensitivity of the method was 0.001 ppm organochlorine pesticides and 0.01 ppm PCBs, on a wet-weight basis. For practical purposes, values lower than 0.01 ppm are not reported since the present mode of confirmation by differential gas chromatography (GC) or GC/mass spectrometry (MS) was not applicable at lower concentrations. Recoveries at concentrations of 0.1–1.0 ppm were above 90 percent except for HCB, for which they were 60 percent. Only HCB residues were corrected for recovery. As part of general quality control during the study, authors participated in several check sample programs, including those conducted by the Canada Committee on Pesticide Usage in Agriculture and the Organization for Economic Cooperation and Development.

MERCURY

Total mercury in 1970–73 samples was determined by wet digestion followed by flameless atomic absorption spectrophotometry (AAS) (*10*). About 0.5 g of the homogenate was weighed into a 50-ml Erlenmeyer flask to which 10 ml concentrated sulfuric acid was added. The flask was placed in a hot water shaker bath until everything dissolved. The cooled mixture was oxidized by the addition of 15 ml of 6 percent potassium permanganate ($KMnO_4$).

AAS was performed on a Varian Techtron Model AA–120 spectrophotemeter as follows: Excess $KMnO_4$ was reduced by the dropwise addition of 20 percent aqueous hydroxylamine hydrochloride; the solution was diluted to 50 ml with distilled water. The dilute solution was placed in a Drechsel gas washing bottle with 1 ml 40 percent tin dichloride and, by use of the air purging method, absorption at 2537A was read. Authors used a mercury hollow cathode lamp as an energy source and a 15-cm-long absorption cell. Curve height was monitored on a Varian Model G2500 recorder and compared with a standard curve. The 1976 samples were analyzed in essentially the same manner except that absorption was read by use of Pharmacia Fine Chemicals Ultraviolet Mercury Monitor equipped with a 30-cm-long absorption cell. Sensitivity of the present method was 0.005 $\mu$g mercury. When 0.5 g of tissue was used, sensitivity was as low as 0.01 ppm. Many comparative studies have shown that the present method is reliable within ± 10 percent of the actual value, and spiked samples showed essentially total recoveries (*10*).

## *Results and Discussion*

Organochlorine and mercury concentrations in the eggs of Leach's storm-petrel, double-crested cormorant, common eider, common tern, alcids other than Atlantic puffin, and Atlantic puffin are given in Tables 1–6,

TABLE 1. *Organochlorine and mercury concentrations in Leach's storm-petrel eggs collected in eastern Canadian coastal waters, 1972–76*

| Site (Map Reference) | Year | No. of Eggs | Arithmetic Mean | | Geometric Mean (Range), ppm Wet Weight | | | | Ratio of PCB/DDE |
|---|---|---|---|---|---|---|---|---|---|
| | | | % Fat | % Moisture | DDE | PCBs | Dieldrin | Mercury | |
| Kent Island (24) | 1972 | 5 | 16.8 | 69.2 | 6.81 (4.61–8.38) | 11.1 (7.51–15.4) | 0.05 (0.05–0.07) | 0.30 (0.26–0.35) | 1.6 |
| | 1976 | 5 | 10.3 | 74.1 | 1.75 (1.37–2.35) | 3.45 (2.80–4.66) | 0.04 (0.03–0.05) | 0.38 (0.25–0.51) | 2.0 |
| Great Island (10) | 1972 | 4 | 17.0 | 68.2 | 2.48 (1.19–8.35) | 2.68 (1.81–4.04) | 0.07 (0.05–0.13) | 0.32 (0.26–0.45) | 1.1 |
| | 1976 | 4 | 7.3 | 73.7 | 0.75 (0.52–1.69) | 1.92 (1.37–5.06) | 0.04 (0.03–0.07) | 0.39 (0.31–0.48) | 2.6 |

TABLE 2. *Organochlorine and mercury concentrations in double-crested cormorant eggs collected in eastern Canadian coastal waters, 1970–76*

| Site (Map Reference) | Year | No. of Eggs | Arithmetic Mean | | Geometric Mean (Range), ppm Wet Weight | | | | Ratio of PCB/DDE |
|---|---|---|---|---|---|---|---|---|---|
| | | | % Fat | % Moisture | DDE | PCBs | Dieldrin | Mercury | |
| Riorden (13) | 1970 | 5 | 4.3 | 84.3 | 8.57 (4.82–17.7) | 8.17 (5.10–19.7) | 0.12 (0.05–0.59) | 0.50 (0.40–0.60) | 1.0 |
| Heron Island (11) | 1970 | 10 | 3.8 | 84.6 | 5.93 (1.11–18.8) | 8.63 (1.34–30.2) | 0.15 (0.01–0.68) | 0.27 (0.10–0.51) | 1.4 |
| | 1973 | 5 | 4.4 | 83.9 | 7.37 (4.03–17.9) | 14.3 (9.86–26.1) | 0.21 (0.14–0.27) | 0.32 (0.26–0.44) | 1.9 |
| Watshishu (5) | 1972 | 5 | 6.3 | 85.1 | 7.56 (2.15–14.8) | 13.8 (5.44–24.3) | 0.19 (0.05–0.31) | 0.34 (0.27–0.48) | 1.8 |
| Ile Ste-Marie (6) | 1972 | 10 | 7.7 | 83.8 | 4.99 (2.50–10.6) | 9.45 (3.00–20.2) | 0.12 (0.05–0.34) | 0.25 (0.15–0.36) | 1.9 |
| Pictou (19) | 1972 | 5 | 3.6 | 83.1 | 4.21 (2.52–7.84) | 11.4 (4.56–22.7) | 0.15 (0.11–0.33) | 0.26 (0.20–0.35) | 2.7 |
| Magdalen Islands (16) | 1973 | 5 | 4.6 | 84.0 | 7.44 (3.76–13.6) | 19.3 (7.13–59.5) | 0.16 (0.08–0.26) | 0.30 (0.20–0.52) | 2.6 |
| Cape Tryon (17) | 1973 | 5 | 4.7 | 83.8 | 5.93 (2.56–11.0) | 11.8 (3.67–21.0) | 0.20 (0.06–0.30) | 0.25 (0.19–0.31) | 2.0 |
| Ile-aux-Pommes (1) | 1972 | 5 | 2.0 | 85.3 | 2.85 (0.18–12.8) | 11.5 (4.62–22.7) | 0.12 (0.08–0.39) | 0.32 (0.26–0.40) | 4.0 |
| | 1976 | 5 | 3.1 | 83.6 | 2.18 (1.16–3.25) | 14.3 (9.13–18.7) | 0.07 (0.02–0.17) | 0.36 (0.16–0.54) | 6.6 |
| Manawagonish Island (25) | 1972 | 10 | 9.9 | 83.2 | 6.51 (3.46–20.0) | 14.6 (9.88–22.3) | 0.15 (0.05–0.36) | 0.22 (0.14–0.39) | 2.2 |
| | 1976 | 5 | 3.8 | 83.1 | 1.49 (0.48–3.15) | 6.31 (2.73–11.9) | 0.06 (0.01–0.17) | 0.24 (0.10–0.50) | 4.2 |
| Boot Island (26) | 1972 | 5 | 4.0 | 83.7 | 4.41 (2.16–13.1) | 8.45 (6.13–22.3) | 0.14 (0.08–0.44) | 0.27 (0.17–0.52) | 1.9 |
| | 1976 | 5 | 3.5 | 83.0 | 1.66 (1.08–2.44) | 5.66 (1.62–9.65) | 0.07 (0.03–0.13) | 0.25 (0.19–0.44) | 3.4 |
| Campbell Island (21) | 1976 | 5 | 4.0 | 83.6 | 1.61 (1.23–2.68) | 9.71 (7.79–11.5) | 0.10 (0.07–0.14) | 0.21 (0.15–0.26) | 6.0 |

TABLE 3. *Organochlorine and mercury concentrations in common eider eggs collected in eastern Canadian coastal waters, 1972*

| Site (Map Reference) | Year | No. of Eggs | Arithmetic Mean | | Geometric Mean (Range), ppm Wet Weight | | | | Ratio of PCB/DDE |
|---|---|---|---|---|---|---|---|---|---|
| | | | % Fat | % Moisture | DDE | PCBs | Dieldrin | Mercury | |
| Inner Birch Island (3) | 1972 | 5 | 17.6 | 66.7 | 0.38 (0.17–0.54) | 1.83 (0.45–3.17) | 0.02 (0.01–0.03) | 0.08 (0.05–0.21) | 4.8 |
| Watshishu (5) | 1972 | 5 | 21.1 | 66.7 | 0.29 (0.25–0.34) | 0.52 (0.36–0.67) | 0.01 (0.01–0.01) | 0.08 (0.05–0.12) | 1.8 |
| Ile Ste-Marie (6) | 1972 | 10 | 21.4 | 66.0 | 0.29 (0.21–0.69) | 0.57 (0.35–2.03) | 0.01 (ND–0.02) | 0.03 (0.01–0.06) | 2.0 |
| Low Duck Island (23) | 1972 | 5 | 16.6 | 66.4 | 0.59 (0.36–0.96) | 4.67 (1.94–30.0) | 0.02 (0.01–0.04) | 0.05 (0.04–0.09) | 7.9 |

NOTE: ND = not detected = $<0.001$ ppm.

TABLE 4. *Organochlorine and mercury concentrations in common tern eggs collected in eastern Canadian coastal waters, 1970–73*

| Site (Map Reference) | Year | No. of Eggs | Arithmetic Mean | | Geometric Mean (Range), ppm Wet Weight | | | | Ratio of PCB/DDE |
|---|---|---|---|---|---|---|---|---|---|
| | | | % Fat | % Moisture | DDE | PCBs | Dieldrin | Mercury | |
| Bathurst (12) | 1970 | 10 | 9.6 | 77.1 | 0.88 (0.70–1.61) | 1.99 (1.12–6.93) | 0.04 (0.03–0.11) | —[1] | 2.3 |
| | 1972 | 10 | 13.3 | 76.0 | 0.62 (0.45–1.19) | 1.96 (1.17–4.79) | 0.03 (0.01–0.05) | 0.12 (0.08–0.20) | 3.2 |
| | 1973 | 10 | 7.8 | 76.8 | 0.49 (0.26–0.61) | 1.48 (0.90–2.09) | 0.02 (0.01–0.05) | 0.08 (0.04–0.14) | 3.0 |
| Tabusintac (14) | 1973 | 5 | 8.6 | 76.0 | 0.52 (0.37–0.61) | 1.37 (1.22–1.61) | 0.03 (0.01–0.05) | 0.06 (0.04–0.10) | 2.6 |
| Magdalen Islands (16) | 1973 | 5 | 9.1 | 76.8 | 0.54 (0.15–1.52) | 1.95 (1.33–3.23) | 0.08 (0.04–0.13) | 0.11 (0.08–0.17) | 3.6 |
| Charlottetown (18) | 1973 | 5 | 8.5 | 76.2 | 1.11 (0.80–3.36) | 1.95 (0.77–3.91) | 0.05 (0.03–0.11) | 0.16 (0.08–0.31) | 1.8 |
| Margaree Island (20) | 1973 | 5 | 9.6 | 76.3 | 0.95 (0.44–1.44) | 1.86 (1.15–2.59) | 0.04 (0.03–0.06) | 0.09 (0.07–0.15) | 1.9 |

[1] Not examined for mercury.

respectively. Lipid and moisture content are also given. Because of the strongly skewed distribution of residue levels, residue data are given as geometric means. The unskewed distribution of fat and moisture data allows their more conventional presentation as arithmetic means.

Organochlorine pesticide and other pollutant concen-

TABLE 5. *Organochlorine and mercury concentrations in eggs of the razorbill, common murre, and black guillemot from eastern Canadian coastal waters, 1971–73*

| Site (Map Reference) | Year | No. of Eggs | Arithmetic Mean | | Geometric Mean (Range), ppm Wet Weight | | | | Ratio of PCB/DDE |
|---|---|---|---|---|---|---|---|---|---|
| | | | % Fat | % Moisture | DDE | PCBs | Dieldrin | Mercury | |
| **RAZORBILL** | | | | | | | | | |
| Carrousel Island (2) | 1972 | 5 | 14.4 | 71.4 | 4.54 (2.30–14.9) | 21.7 (12.8–37.3) | 0.15 (0.08–0.52) | 0.08 (0.01–0.19) | 4.8 |
| Ile Ste-Marie (6) | 1972 | 5 | 17.2 | 72.4 | 2.75 (1.82–3.28) | 9.34 (6.29–15.0) | 0.10 (0.06–0.15) | 0.12 (0.08–0.15) | 3.4 |
| Brion Island (15) | 1973 | 3 | 12.5 | 72.0 | 2.55 (2.14–3.10) | 8.37 (7.72–12.1) | 0.12 (0.01–0.16) | 0.11 (0.04–0.25) | 3.3 |
| **COMMON MURRE** | | | | | | | | | |
| Ile Ste-Marie (6) | 1971 | 4 | 17.0 | 67.6 | 2.03 (1.28–3.81) | 2.21 (0.94–7.00) | 0.02 (0.02–0.03) | 0.12 (0.08–0.17) | 1.1 |
| **BLACK GUILLEMOT** | | | | | | | | | |
| Magdalen Islands (16) | 1973 | 3 | 9.9 | 73.8 | 1.04 (0.75–1.27) | 2.13 (2.06–3.82) | 0.02 (0.01–0.05) | 0.13 (0.10–0.17) | 2.0 |

TABLE 6. *Organochlorine and mercury concentrations in Atlantic puffin eggs collected in eastern Canadian coastal waters, 1972–76*

| Site (Map Reference) | Year | No. of Eggs | Arithmetic Mean | | Geometric Mean (Range), ppm Wet Weight | | | | Ratio of PCB/DDE |
|---|---|---|---|---|---|---|---|---|---|
| | | | % Fat | % Moisture | DDE | PCBs | Dieldrin | Mercury | |
| Betchouane (4) | 1972 | 5 | 16.2 | 71.4 | 1.19 (0.75–2.28) | 4.42 (2.76–7.40) | 0.06 (0.05–0.10) | 0.15 (0.10–0.22) | 3.7 |
| Ile Ste-Marie (6) | 1972 | 9 | 16.7 | 71.1 | 0.99 (0.62–1.72) | 2.89 (1.20–5.11) | 0.06 (0.04–0.10) | 0.16 (0.07–0.24) | 2.9 |
| Perroquet Island (7) | 1972 | 5 | 14.8 | 69.9 | 1.49 (1.22–1.70) | 3.99 (3.08–5.08) | 0.07 (0.05–0.09) | 0.16 (0.08–0.20) | 2.7 |
| Gannet Island (8) | 1972 | 5 | 13.7 | 70.7 | 0.57 (0.43–0.73) | 2.32 (1.69–2.90) | 0.05 (0.04–0.06) | 0.18 (0.16–0.21) | 4.1 |
| Bird Island (9) | 1972 | 5 | 17.5 | 72.0 | 0.58 (0.48–0.90) | 1.90 (1.48–3.06) | 0.04 (0.03–0.05) | 0.18 (0.10–0.34) | 3.3 |
| Brion Island (15) | 1973 | 1 | 10.2 | 73.2 | 1.46 | 4.19 | 0.06 | 0.16 | 2.9 |
| Great Island (10) | 1972 | 3 | 15.8 | 68.7 | 0.76 (0.52–0.89) | 1.67 (1.49–1.99) | 0.05 (0.04–0.06) | 0.26 (0.21–0.33) | 2.2 |
| | 1976 | 5 | 10.2 | 71.5 | 0.59 (0.43–0.87) | 1.86 (1.63–2.00) | 0.04 (0.04–0.05) | 0.23 (0.14–0.28) | 3.2 |
| Machias Seal Island (22) | 1972 | 5 | 13.0 | 71.5 | 2.57 (1.97–3.89) | 7.20 (5.80–8.19) | 0.09 (0.07–0.11) | 0.20 (0.18–0.26) | 2.8 |
| | 1976 | 5 | 11.3 | 70.7 | 1.27 (0.75–1.76) | 6.10 (4.73–6.59) | 0.08 (0.06–0.13) | 0.09 (0.06–0.12) | 4.8 |

trations in eggs can be adjusted for loss of lipid and moisture during incubation (*30*). The problem of how best to express organochlorine residues in homogenized avian eggs has been further addressed by Peakall and Gilman (*25*). They showed that in the herring gull (*Larus argentatus*) the lipid and moisture contents of the combined yolk and albumin remain fairly constant over the incubation period, as do lipid and moisture contents of the developing embryo. The yolk-plus-albumin:embryo ratio shifts continuously as the embryo grows. The lipid content of the total egg decreases to one fifth during incubation, and the moisture content decreases to about four fifths. One can conclude from the data of Peakall and Gilman (*25*) that, where stage of incubation varies from sample to sample, comparisons of residues of whole egg contents will be more accurate on a wet-weight than on a lipid-weight basis. Moisture content of samples in the present study varied little within species, and residue data are expressed on a wet-weight basis.

In the present study, all organochlorine residues except DDE and PCBs are low in all samples. Mean DDE ranged from 0.29 ppm in common eider to 8.57 ppm in double-crested cormorant. Mean PCBs ranged from 0.52 ppm in common eider to 21.7 ppm in razorbill. Authors found TDE and *p,p'*-DDT in most samples frequently at $< 0.01$ ppm and $< 0.10$ ppm, respectively, *p,p'*-DDT exceeded 0.10 ppm only in eggs of Leach's storm-petrel, mean concentrations being 0.33 ppm and 0.39 ppm in Kent Island eggs in 1972 and 1976, respectively, and 0.17 ppm and 0.15 ppm in eggs from Great Island in 1972 and 1976, respectively. Dieldrin was present in most eggs. The highest concentration, 0.68 ppm, was found in eggs of the double-crested cormorant collected in 1970 on Heron Island. HCB was found in all eggs, corrected residue concentrations being $< 0.10$ ppm except in alcids, in which they ranged to 0.23 ppm in razorbill and puffin, and to 0.27 ppm in murre. Heptachlor epoxide occurred at low concentrations in most eggs, exceeding 0.05 ppm in

less than 5 percent of the total. Endrin was found only in 1972 samples, at $< 0.10$ ppm except in the eggs of razorbill in which it ranged from 0.10 to 0.21 ppm. *cis*-Chlordane and oxychlordane residues of $< 0.10$ ppm were found in all eggs in 1976, but only in that year. The lowest mean mercury concentration, 0.03 ppm, was noted in common eider eggs collected in 1972 at Ile Ste-Marie. The highest mean mercury level, 0.50 ppm, was recorded for double-crested cormorant eggs collected in 1970 at Riorden.

DDE and PCB concentrations in the eggs of several species collected in the Bay of Fundy were compared. Although Leach's storm-petrel is pelagic and feeds on small crustaceans and cephalopods (*21*) at low trophic levels, eggs of that species contained the highest residues. Presumably that is because petrels feed at the interface of the air and water where organochlorines first reach the oceans and where they may be held by a thin oily film on the surface.

The relatively high organochlorine concentrations in cormorants would be expected; cormorants eat fish of considerable size and are essentially coastal. Other Bay of Fundy double-crested cormorant colonies were reported to be more heavily contaminated in 1971 (*35*) than those sampled in the present study. When compared on a lipid-weight basis, DDE and PCB residues in double-crested cormorant eggs from most of the sites sampled in the present study were higher than those reported in eggs of that species from the Strait of Georgia, British Columbia (*20*).

Residues were low in eider eggs, despite the predominance in their diet of mollusks (*22*), which are considered to be good accumulators of chemical pollutants (*26*) and which may reflect local levels of contamination where exposure is chronic. At Ile Ste-Marie, in the Gulf of St. Lawrence, residues were highest in double-crested cormorants and lowest in eiders; no petrel eggs were collected there. Among the Alcidae at that site, residues were highest in the razorbill, and lowest in the Atlantic puffin. As with organochlorines, mercury concentrations were lowest in eiders and terns, intermediate in alcids, and highest in cormorants and petrels.

Changes in contaminant concentrations in eggs between 1972 and 1976 can be compared in three species at six sites: Leach's storm-petrel at Kent Island and Great Island; double-crested cormorant at Manawagonish Island, Boot Island, and Ile-aux-Pommes; and Atlantic puffin at Machias Seal Island and Great Island. In all cases DDE residues decreased, but significantly only in petrels at Kent Island ($P < 0.01$), puffins at Machias Seal Island ($P < 0.01$), and cormorants at Manawagonish Island ($P < 0.05$). PCB concentrations decreased significantly ($P < 0.01$) in petrels at Kent Island and cormorants at Manawagonish Island but increased significantly ($P < 0.01$) in puffins at Great Island. The ratio of PCBs to DDE increased between 1972 and 1976 in all cases, indicating that DDE concentrations in the foods of those birds decreased more rapidly than PCB concentrations. There was little indication of changes in mercury contamination of the eggs over that time period. Authors feel that the above-reported analytical refinements were minor and do not invalidate comparisons of changes in residue concentrations over time.

DDE and PCB residues in Atlantic puffin eggs collected from the Bay of Fundy were considerably higher ($P < 0.01$) in 1972 and 1976 than residues in eggs from an open-ocean colony off Newfoundland. Wintering areas of puffins inhabiting those colonies are unknown, and females returning there from the open ocean may not carry equivalent contaminant loads. If contaminant loads of such birds were equivalent the uptake of organochlorines between arrival of females and egg formation, a period of about four weeks in Great Britain (*17*), would have to be much more rapid in the Bay of Fundy, presumably reflecting a more contaminated environment there. In the present study, DDE residues in Leach's storm-petrel eggs were also higher in the Bay of Fundy than they were in Newfoundland in 1972 ($P < 0.05$) and in 1976 ($P < 0.01$). Again, the interval between arrival at the colony and egg laying was about a month (*21*).

TABLE 7. *DDE concentrations associated with 20% eggshell thinning in the eggs of Procellariiformes, Pelecaniformes, Ciconiiformes, and Charadriiformes*

| Species | DDE, ppm Wet Weight | Reference |
|---|---|---|
| Procellariiformes | | |
| Leach's storm-petrel (*Oceanodroma leucorhoa*) | 12[1] | This study |
| Pelecaniformes | | |
| Brown pelican (*Pelecanus occidentalis*) | 8 | (*3*) |
| Gannet (*Morus bassanus*) | 11[2] | (*23*) |
| Great cormorant (*Phalacrocorax carbo*) | 10 | (*15*) |
| Double-crested cormorant (*Phalacrocorax auritus*) | 10 | This study |
| Ciconiiformes | | |
| Great blue heron (*Ardea herodias*) | 47[3] | (*9*) |
| Grey Heron (*Ardea cinerea*) | 25 | (*5*) |
| Charadriiformes | | |
| Herring gull (*Larus argentatus*) | 160[4] | (*32*) |
| Common tern (*Sterna hirundo*) | 25 | (*31*) |
| Razorbill (*Alca torda*) | 45[1] | This study |
| Atlantic puffin (*Fratercula arctica*) | 30[1] | This study |

[1] Extrapolated. Linear regressions were used and correlation coefficients were calculated using the Pearson product-moments formula.
[2] Assuming 10 percent lipid.
[3] Assuming 10 percent lipid, level associated with 16 percent thinning.
[4] Assuming water content of 80 percent.

In the present study, DDE and PCB residues in razorbill eggs were one to two orders of magnitude lower than residues in razorbill eggs collected from the Baltic Sea in 1970–72 (*2*). DDE and PCB levels in Atlantic puffin eggs from the colonies in Newfoundland-Labrador were high compared to samples collected at St. Kilda in 1969 (*24*). DDE residues in Leach's storm-petrel eggs from Kent Island and Great Island in 1968 (*14*) were similar to 1972 samples in the present study and reflect the same contrast between sites. When compared on a lipid-weight basis, DDE concentration in Leach's storm-petrel eggs from the west coast of Vancouver Island in 1970 (*20*), the only other literature value apparently available, was similar to the values reported here, but the present PCB residues were considerably higher. DDE and PCB concentrations in the eggs of the fork-tailed storm-petrel (*O. furcata*) from the Queen Charlotte Islands (*20*) were similar to the values reported here, but DDE residues in ashy storm-petrel (*O. homochroa*) eggs from the California coast (*6*) were much higher.

The significance of elevated mercury concentrations in marine birds is not yet known. The most serious effect of DDE on the reproduction of birds is eggshell thinning, which has been demonstrated in a variety of species (*4*). Laboratory experiments and field investigations indicate that, in the absence of effects caused by eggshell thinning, high concentrations of organochlorines are required to impair reproductive success. Herring gulls on Lake Huron and Lake Superior reproduce normally despite residues of 15–20 ppm DDE and 50–60 ppm PCBs in their eggs (*11*), whereas double-crested cormorants showed severe declines and severe eggshell thinning at 7–11 ppm DDE and 10–12 ppm PCBs (*27*). DDE caused eggshell thinning in the double-crested cormorant in prairie states and provinces, and was related to a severe colony decline in Wisconsin (*1*). Laboratory studies have shown that most organochlorines are relatively nontoxic when injected into chicken eggs at concentrations up to 250 ppm (*8*).

The DDE concentration associated with eggshell thinning varies greatly among species. Residues of DDE associated with 20 percent eggshell thinning, considered to be the population damage threshold, have been calculated for six species (*14*). That amount of thinning has been correlated with population declines of several species of fish-eating and raptorial birds (*13*). In Table 7 the published data relating DDE in eggs to 20 percent eggshell thinning in aquatic birds are summarized.

Eggshell thickness indices were plotted against DDE concentrations in eggs. For the Leach's storm-petrel, in which the relationship showed a correlation coefficient of −0.74, extrapolation of the regression analysis indicates that 12 ppm DDE (wet weight) would be expected to be associated with 20 percent eggshell thinning. Although Leach's storm-petrel is apparently sensitive to DDE, that level of contamination was not reached in any of the eggs of that species taken during the present survey. In the case of the double-crested cormorant, 10 ppm DDE was related to 20 percent eggshell thinning, a value which corresponds well with those found by other investigators for the double-crested cormorant (*1, 12*) and closely related species (*15*). DDE residues exceeded 10 ppm in one-fifth of the cormorant eggs analyzed in the present study. Regression plots of eggshell thickness indices against DDE for two species of Alcidae, the razorbill and the Atlantic puffin, gave low correlation coefficients of −0.40 and −0.47, respectively. The razorbill sample was small, DDE exceeding 5 ppm in only one egg. The occurrence of significant eggshell thinning could not be related to much higher levels of ΣDDT in razorbill eggs from the Baltic Sea (*2*). The present Atlantic puffin data varied significantly, like data on the common tern (*31*). It appears that alcids, like other members of the Charadriiformes (*13, 32*), are relatively insensitive to DDE.

Authors conclude that among the species investigated some populations of double-crested cormorants probably have been adversely affected by DDE, through shell thinning, and that the margin of safety for Leach's storm-petrel is narrow. The other species investigated probably were unaffected.


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# *Residues of Polychlorinated Biphenyls and DDT in Water and Sediment of the St. Lucie Estuary, Florida, 1977*[1]

Tsen C. Wang, Joseph P. Krivan, Jr., and Robert S. Johnson


## ABSTRACT

*ΣDDT residues in the St. Lucie River bottom sediments increased after Lake Okeechobee water was discharged through the St. Lucie Canal into the area. ΣDDT levels were highest in sediment samples from the Palm City area, ranging from 1.8 ppb to 6.15 ppb. Sediment samples from the A1A Highway Bridge area contained 1.6–6.8 ppb Aroclor 1254. Levels of polychlorinated biphenyls (PCBs) and ΣDDT in sediment samples from the junction of the St. Lucie and Indian Rivers were not detectable. Surface water samples from the estuary did not show any detectable DDT or PCB residues.*


## *Introduction*

The St. Lucie Estuary is a tidewater at the junction of the North and South Forks of the St. Lucie River near Stuart, Martin County, Florida (Fig. 1). The main river empties into the Atlantic Ocean through the St. Lucie Inlet. The Indian River, a shallow lagoon, flows across the St. Lucie River and also discharges into the St. Lucie Inlet. The St. Lucie Canal leaves Lake Okeechobee at Port Mayaca and extends to the South Fork of the St. Lucie River at Stuart. Lake Okeechobee water released through the St. Lucie Canal carries fine sand, shell fragments, and organic material into the St. Lucie Estuary (*3*). Runoff from the canal could introduce organochlorine and organophosphorus insecticides into the estuary aquatic environment (*6, 7, 9*). The purpose of this work was to survey polychlorinated biphenyls (PCBs) and ΣDDT in water and sediments of the St. Lucie Estuary.

## *Sampling and Analysis*

Samples of surface water and sediment were collected at different locations on the river as shown in Figure 1. Samples were taken June 14, June 21, and July 8, 1977.

Grab water samples were collected in one gallon glass solvent bottles that had been cleaned with chromic acid, acetone, and methylene chloride. Three liters of each sample was drained through a glass column containing 50 ml Amberlite XAD-2 resin (*4*) at 250 ml/minute. The column was eluted with 200 ml acetonitrile at full gravity flow, followed by 500 ml distilled water. The combined eluate was then extracted with hexane. The water extracts were cleaned on a Florisil microcolumn (*8*) before gas chromatographic analysis.

A copper core sampler was used to take the sediment samples. Three samples, collected from each station on the river, were composited and subsampled for analysis. The 100-g subsamples were extracted with isopropyl alcohol–hexane solvent. The sediment was extracted first in isopropyl alcohol and then in hexane to recover the isopropyl alcohol together with desorbed material. The extract was washed with distilled water, filtered through a sodium sulfate–Celite column, and concentrated to 1 ml before cleanup (*13*). The hexane extract was then passed through a Florisil column, and the first fraction was passed through a silicic acid column to separate PCBs from the chlorinated pesticides (*2*). Activated copper foil was added to the first fraction to remove any sulfur from the bottom sediment extracts before they were applied to the silicic acid column (*5, 12*). Residues in the samples were further treated with potassium hydroxide for confirmation and sample cleanup (*1, 14*).

Compounds were identified by electron-capture gas chromatography on dual columns packed with 1.5 percent OV-17 plus 1.95 percent QF-1 and 4 percent SE-30 plus 6 percent OV-210 solid support. Samples of sufficient size and concentration were confirmed by thin-layer chromatography (*11*). PCBs and ΣDDT were quantified by matching the unknown peaks on the chromatogram to the standard samples. Lower detection limits for PCBs and ΣDDT were 0.5 ppb and 0.01 ppb in water and 0.10 ppb and 1.0 ppb in bottom sediment, respectively. After water and sediment samples were collected from the St. Lucie River, duplicate residue analyses were performed. The arithmetic means of PCB and ΣDDT concentrations for each sediment sample are presented in Table 1.

[1]Harbor Branch Foundation, Inc., Rural Route 1, Box 196, Fort Pierce, Fla. 33450. Harbor Branch Contribution No. 148.

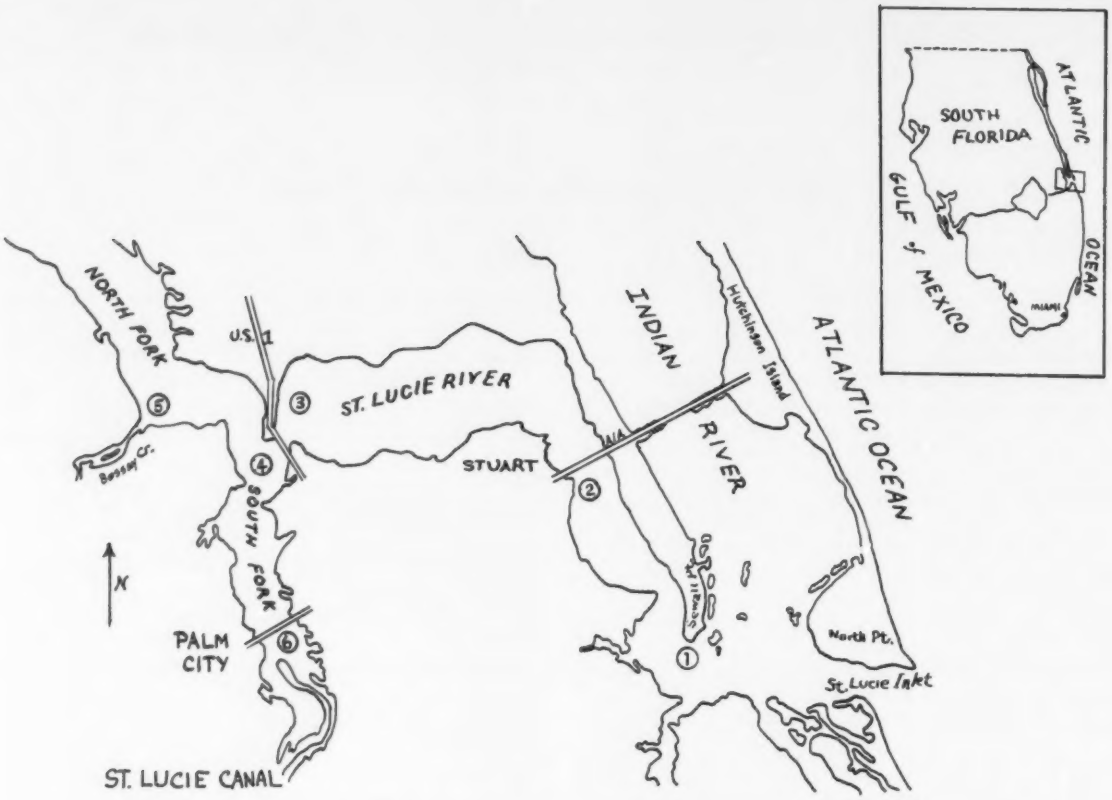


FIGURE 1. *Sampling stations on the St. Lucie Estuary, Florida, 1977 (See Table 1 for key identification.)*

### *Results and Discussion*

Three sets of water and sediment samples collected on different dates were analyzed. The results are shown in Table 1. Sediment samples from Station 2, near Highway A1A bridge, contained 1.6–6.8 ppb Aroclor 1254. This area could be locally contaminated by any PCB-containing fluids or formulations such as hydraulic fluids, plasticizers, lubricants, heat exchanger electric transformers, insulators, paints, or sealing compounds (*10*). No PCBs were found at any of the other sampling stations.

As shown in Table 1, ΣDDT levels were higher in the second and third sets of samples than in the first set. On June 20, 1977, the St. Lucie Canal discharged water from Lake Okeechobee through the St. Lucie River at a rate of 1,000 ft³/minute. The second set of samples was collected during the second day that the canal water was being discharged into the estuary. The third set of samples was collected during the last two days of the discharging schedule. The higher concentration of DDT compounds in the second and third sets of samples could be due to runoff from the canal.

Highest ΣDDT levels were 1.8–6.15 ppb in samples from Station 6, near the Palm City Bridge. Significant ΣDDT levels were found in sediment samples as follows: from the junction of Bessey Creek and North Fork, 0.2–1.69 ppb; from the junction of South Fork and North Fork, 0.85 ppb; near Highway US1, 0.09–0.68 ppb; and near A1A Bridge, 0.6–1.09 ppb. In samples from Station 1, about 15 miles from Palm City, DDT and PCBs were not detectable.

Three sets of surface water samples were also collected and analyzed. PCBs and DDT were not found in the water samples.

TABLE 1. *Residues of polychlorinated biphenyls and ΣDDT in sediment of the St. Lucie Estuary, Florida, 1977*

| Sample Number | Sampling Station Area | Detectable Compounds | Arithmetic Mean Residues, ppb | | |
|---|---|---|---|---|---|
| | | | June 14, 1977 | June 21, 1977 | July 8, 1977 |
| 1 | Junction of the St. Lucie and Indian Rivers | | DDT & PCBs were not detected | | |
| 2 | Highway A1A Bridge | Aroclor 1254 | 6.8 | 1.6 | 4.6 |
| | | *p,p'*-TDE | 0.6 | 0.25 | 0.89 |
| | | *p,p'*-DDE | ND | 0.56 | 0.20 |
| | | ΣDDT | 0.6 | 0.81 | 1.09 |
| 3 | Highway U.S. 1 Bridge | *o,p'*-DDE | ND | 0.17 | ND |
| | | *p,p'*-DDE | 0.09 | 0.29 | 0.31 |
| | | *p,p'*-TDE | ND | 0.22 | 0.19 |
| | | ΣDDT | 0.09 | 0.68 | 0.50 |
| 4 | Junction of South and North Forks | *o,p'*-DDE | — | 0.53 | ND |
| | | *p,p'*-DDE | — | 0.18 | 0.53 |
| | | *p,p'*-TDE | — | 0.15 | 0.32 |
| | | ΣDDT | — | 0.86 | 0.85 |
| 5 | Bessey Creek, North Fork | *o,p'*-DDE | ND | 0.53 | ND |
| | | *p,p'*-DDE | 0.2 | 0.73 | 0.16 |
| | | *o,p'*-TDE | ND | 0.13 | ND |
| | | *p,p'*-TDE | ND | 0.30 | 0.14 |
| | | ΣDDT | 0.2 | 1.69 | 0.30 |
| 6 | Palm City Bridge, South Fork | *o,p'*-DDE | ND | 0.92 | 0.52 |
| | | *p,p'*-DDE | ND | 0.94 | 0.83 |
| | | *o,p'*-TDE | ND | 0.24 | 0.30 |
| | | *p,p'*-TDE | 1.8 | 0.75 | 1.10 |
| | | *o,p'*-DDT | ND | ND | 1.10 |
| | | *p,p'*-DDT | ND | ND | 2.30 |
| | | ΣDDT | 1.8 | 2.85 | 6.15 |

NOTE: ND = not detected.

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# SOILS

## *Dicofol Residues in United States Soils Having a Known History of Its Use as a Miticide, 1974*

William R. Lyman [1] and Rollin J. Anderson [2]

ABSTRACT

*Soil samples were collected from a total of 21 sites in California, Washington, Florida, Pennsylvania, and Michigan. Dicofol (Kelthane) miticide had been applied at various times over a 5-year period to 17 of the sites; four sites had received no applications. Samples were collected at 0–75-mm and 75–150-mm depths, and submitted to gas-liquid chromatographic analysis. Samples from only four of the 17 treated sites contained mean residues equal to or exceeding 2.00 ppm. Residues in all cases were only a small fraction of the total amount applied. Apparently, a mechanism for the dissipation of dicofol exists, but it is unidentified at this time.*

### *Introduction*

Dicofol is marketed as a miticide under the trade name Kelthane. In laboratory studies, dicofol has shown little tendency toward microbial degradation or migration in soil through leaching (Rohm and Haas Co., unpublished data: 1978). It is subject to some photolytic degradation and, under alkaline conditions, breaks down readily to yield chloroform and 4,4′-dichlorobenzophenone. Studies have shown that dicofol residues are low compared to residues of DDT and other organochlorine insecticides (*2–6, 8–10*). Harris and Sans confirmed that residues tend to remain near the surface (*3*). In general, however, no information was given on the amounts applied. When such information was provided, the amounts applied were relatively low. This paper reports the results of analyses of soil samples collected during 1974 from sites where the history of dicofol usage was known. Sites represented widely separated geographical locations within the United States and five different categories of use history. A range of soil types resulted incidentally.

### *Sample Collection*

Through Rohm and Haas Company field sales representatives and their contacts with growers, distributors, and spray applicators, growers were sought who had records of the amounts and timing of dicofol applications to their crops or orchards over a period of years. In this way a total of 17 sites in California, Washington, Florida, Pennsylvania, and Michigan were selected. Sites were chosen in five use history categories as follows: dicofol applied for five or more successive years including 1973; dicofol applied for several successive years including 1972, but not in 1973; dicofol applied for several successive years but not later than 1971; dicofol applied in 1973, but not previously; no known use of dicofol.

Most sites selected were 10–20-ha. apple or citrus orchards. Soil was taken with a core sampler at depths of 0–75 mm and 75–150 mm from ten or more randomly selected spots within each site. The core samplers were 19 mm (¾ inch) in diameter except in Florida sand where a 12-mm (½ inch) sampler was used. The 0–75-mm segments from the various cores were composited as were the 75–150-mm segments. Samples were shipped to the laboratory where they were stored frozen until analysis.

### *Analyses*

A 50-g representative subsample, free of stones, was added to 10 ml water in a one-pint Waring Blendor jar and allowed to stand 30 minutes. The subsample was blended with 50 ml isopropanol for 2 minutes at high speed. Then 100 ml benzene was added, and the mixture was blended for 3 minutes. The mixture was filtered with suction; transfer and rinse were accomplished with a 1:2 mixture of isopropanol–benzene, bringing the final volume to 200 ml. Forty ml of extract, equivalent to 10 g soil, was dried in a rotary vacuum evaporator, and the residue was dissolved in petroleum ether. Florisil was activated by heating overnight for 16 hours in an oven at 100°C, then deactivated by the addition of 8 percent water. The adsorbent was packed into a 1-cm-diameter column to a depth of 10 cm, and topped with 2 cm anhydrous sodium sulfate. The petroleum ether solution was poured onto the column. The flask was rinsed with 10 ml petroleum ether and the column was washed with 20 ml petroleum ether; all effluents were discarded. Dicofol was eluted with 25 ml of 2 percent ethyl ether in petroleum ether. The eluate was evaporated to dryness and dissolved in 1 ml *n*-hexane; 0.5 g anhydrous sodium sulfate was added to absorb moisture.

[1] Agricultural Products Research, Rohm and Haas Co., Spring House, Penn. 19477.
[2] Tracor, Inc., 6500 Tracor Lane, Austin, Tex. 78721.

A 5-$\mu$l aliquot of the solution was injected into the gas chromatograph.

Analysis was performed on a Tracor Model 550 gas chromatograph equipped with a $^{63}$Ni electron-capture detector. Instrument parameters and operating conditions follow:

| | |
|---|---|
| Column: | Pyrex, 1.83 m long x 6.4 mm OD, packed with 10 percent SE-30 on 80–100-mesh Gas-Chrom Q |
| Temperatures: | column 210°C |
| | injector 275°C |
| | detector 305°C |
| Carrier gas: | nitrogen flowing at 60 ml/minute |
| Retention time: | 4.25 minutes |

Under the conditions of analysis described above, dicofol is decomposed quantitatively to 4,4′-dichlorobenzophenone which is the peak measured. During extraction and cleanup, 4,4′-dichlorobenzophenone, if present, is not separated. Thus, the residue measured is the sum of dicofol and dichlorobenzophenone. Each day that analyses were run, known amounts of dicofol standard were injected until the response was stable. Further standard injections were interspersed with injections of samples.

A calibration curve was drawn, plotting peak height versus the amount of standard injected. Dicofol in sample injections was determined from the calibration curve. Recovery throughout the analytical process was measured by fortifications to soil before blending. All data are corrected for recovery which was generally 85–100 percent. Sensitivity was 0.01 ppm.

Confirmatory analyses were not run on the samples. Because residue levels were low, confirmation was less important. Compared to many chlorinated pesticides which might interfere, dicofol (measured as dicholorobenzophenone) has a relatively short retention time on a column such as SE-30 which separates materials mainly according to vapor pressure. This is shown in data of Fishbein (*1*).

## *Results and Discussion*

Data on application, sampling, and analyses are reported in Table 1. Not every sample precisely fits the category to which it is assigned. In about half the cases, three or more replicate samples were provided. In these cases, the average residue is given, along with the range of values among the replicate samples. In one case only, no samples were provided from the 3–6 inch soil depth.

The samples represent a wide range of dicofol usage, from less than 1 kg/ha. applied during 1 year to over 50 kg/ha. applied over 8 years.

The weight of a medium density soil (loam) to a depth of 7 inches over an area of 1 acre has been stated to be approximately 2 million pounds (*7*). Thus, in metric units, the weight of soil to a depth of 75 mm (3 inches) over 1 ha. is $9.6 \times 10^5$ kg. Thus, 1 kg of pesticide applied to 1 ha. should result in an average concentration in soil of 1.04 ppm if distributed to a depth of 75 mm. Plowing and cultivation to a greater depth would proportionately lessen the residue concentration. Table 1 shows the maximum residue concentration to be expected if all of the dicofol applied reached the soil and remained in the top 75 mm. In the last column is given the ratio of the average concentration found to the maximum possible concentration calculated.

No dicofol was detected in soil samples from the four sites which had no history of its use. Samples from only four of the 17 treated sites contained mean residues in the top 75 mm of soil equaling or exceeding 2.00 ppm. In nearly all cases, the amount of dicofol remaining in soil was only a small fraction of the total applied.

The data in Table 1 suggest that the amount of dicofol residue remaining in soil bears no obvious relation to the total amount applied or to the interval between the last application and sampling. However, dicofol may be more persistent in sand than in other soil types.

## *Conclusions*

Although the mechanisms by which dicofol residues are dissipated are not known, it is clear that such mechanisms must exist. The levels of residue found in soils from various locations of known usage history are in line with those reported by other workers in more general and extensive pesticide monitoring studies. These data also confirm that dicofol residues tend to remain near the soil surface.


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TABLE 1. *Dicofol residues in United States soils having a known history of its use, 1974*

| Sample Code | State | Soil Type | Total Dicofol, Kg/Ha | Years Applied | TSI[1], Days | Sample Depth, mm | Residue, ppm | | No. of Reps | Maximum Residue, ppm | Ratio, Found/ Max. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Average | Range | | | |
| **DICOFOL APPLIED FOR SEVERAL YEARS, INCLUDING 1973** | | | | | | | | | | | |
| 74–023 | Calif. | Sandy loam | 53.8 | 66–68, 70–73 | 414 | 0–75 | 1.08 | 0.28–2.86 | 6 | 56.0 | 0.02 |
| 74–027 | Wash. | Clay loam | 5.6 | 69–73 | 276 | 0–75 | 0.98 | | 1 | 5.8 | 0.17 |
| | | | | | | 75–150 | 0.26 | | 1 | | |
| 74–066 | Penn. | Clay | 23.5 | 71–73 | 314 | 0–75 | 2.0 | 1.84–2.30 | 3 | 24.0 | 0.08 |
| | | | | | | 75–150 | 0.43 | 0.22–0.64 | 3 | | |
| 74–181 | Fla. | Sand | 15.0 | 66–71, 73 | 554 | 0–75 | 3.48 | 2.91–4.04 | 3 | 16.0 | 0.21 |
| | | | | | | 75–150 | 0.84 | 0.21–1.90 | 3 | | |
| **DICOFOL APPLIED FOR SEVERAL YEARS, BUT NOT IN 1973** | | | | | | | | | | | |
| 74–014 | Calif. | Clay loam | 7.0 | 67–72 | 665 | 0–75 | 0.09 | 0.00–0.14 | 3 | 7.4 | 0.01 |
| | | | | | | 75–150 | 0.00 | 0.00–0.00 | 3 | | |
| 74–026 | Wash. | Clay loam | 5.6 | 68–72 | 639 | 0–75 | 0.00 | | 1 | 5.8 | 0.00 |
| | | | | | | 75–150 | 0.00 | | 1 | | |
| 74–067 | Penn. | Silt loam | 16.8 | 71–72 | 679 | 0–75 | 0.34 | 0.22–0.42 | 3 | 17.0 | 0.02 |
| | | | | | | 75–150 | 0.26 | 0.11–0.44 | 3 | | |
| 74–154 | Fla. | Sand | 11.2 | 66–72 | 719 | 0–75 | 0.28 | 0.18–0.38 | 3 | 12.0 | 0.02 |
| | | | | | | 75–150 | 0.00 | 0.00–0.00 | 3 | | |
| **DICOFOL APPLIED FOR SEVERAL YEARS, BUT NOT FOR 3 YEARS OR MORE BEFORE SAMPLING IN 1974** | | | | | | | | | | | |
| 74–029 | Wash. | Silt loam | 5.6 | 66–70 | 1384 | 0–75 | 0.28 | | 1 | 5.8 | 0.05 |
| | | | | | | 75–150 | 0.06 | | 1 | | |
| 74–056 | Mich. | Clay loam | 50.4 | 60–69 | 1804 | 0–75 | 0.06 | 0.00–0.19 | 3 | 53.0 | 0.0001 |
| | | | | | | 75–150 | 0.00 | 0.00–0.00 | 3 | | |
| 74–068 | Penn. | Silt loam | —[3] | pre-1969 | 1825 | 0–75 | 1.02 | 0.79–1.16 | 3 | — | — |
| | | | | | | 75–1-50 | 0.60 | 0.29–1.10 | 3 | | |
| 74–153 | Fla. | Sand | 6.55 | 65–69, 71 | 1003 | 0–75 | 3.25 | 1.87–4.14 | 3 | 6.8 | 0.48 |
| | | | | | | 75–150 | 1.13 | 0.23–1.65 | 3 | | |
| **DICOFOL APPLIED IN 1973 ONLY (NONE BEFORE THEN)** | | | | | | | | | | | |
| 74–015 | Calif. | Clay loam | 1.3 | 1973 | 300 | 0–75 | 0.00 | 0.00–0.00 | 3 | 1.4 | 0.00 |
| | | | | | | 75–1-50 | 0.00 | 0.00–0.00 | 3 | | |
| 74–030 | Wash. | Silt loam | 0.9 | 1973 | 259 | 0–75 | 0.12 | | 1 | 0.09 | 0.13 |
| | | | | | | 75–150 | 0.00 | | 1 | | |
| 74–057 | Mich. | Sand | 3.4 | 1973 | 333 | 0–75 | 0.00 | | 1 | 3.5 | 0.00 |
| | | | | | | 75–150 | 0.00 | | 1 | | |
| 74–147 | Fla. | Sand | 4.5 | 1973 | 314 | 0–75 | 0.46 | 0.08–0.75 | 3 | 4.7 | 0.10 |
| | | | | | | 75–150 | 0.00 | 0.00–0.00 | 3 | | |
| 74–148 | Fla. | Sand | 13.4 | 73–74 | 175 | 0–75 | 2.58 | 0.65–4.6 | 3 | 14.0 | 0.18 |
| | | | | | | 75–150 | 0.63 | 0.20–0.94 | 3 | | |
| **NO KNOWN USE OF DICOFOL** | | | | | | | | | | | |
| 74–013 | Calif. | Clay loam | 0.0 | — | — | 0–75 | 0.00 | | 5 | | |
| | | | | | | 75–150 | 0.00 | | 3 | | |
| 74–028 | Wash. | Silt loam | 0.0 | — | — | 0–75 | 0.00 | | 1 | | |
| | | | | | | 75–150 | 0.00 | | 1 | | |
| 74–058 | Mich. | —[3] | 0.0 | — | — | 0–75 | 0.00 | | 1 | | |
| | | | | | | 75–150 | 0.00 | | 1 | | |
| 74–162 | Fla. | Sand | 0.0 | — | — | 0–75 | 0.00 | | 3 | | |
| | | | | | | 75–150 | 0.00 | | 3 | | |

[1] TSI = Treatment until Sampling Interval.
[2] Records of use not available. Dicofol known to have been used prior to 1969.
[3] Information not provided.


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# APPENDIX

## *Chemical Names of Compounds Discussed in This Issue*

| | |
|---|---|
| ALDRIN | Hexachlorohexahydro-*endo, exo*-dimethanonaphthalene 95% and related compounds 5% |
| AROCLOR 1254 | PCB, approximately 54% chlorine |
| AROCLOR 1260 | PCB, approximately 60% chlorine |
| BHC (Benzene Hexachloride) | 1,2,3,4,5,6-Hexachlorocyclohexane (mixture of isomers) |
| CHLORDANE | 1,2,3,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene. The technical product is a mixture of several compounds including heptachlor, chlordene, and two isomeric forms of chlordane. |
| CHLORDENE | 4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methano-1*H*-indene |
| CIODRIN | Dimethyl phosphate of α-methylbenzyl 3-hydroxy-*cis*-crotonate |
| DDE | Dichlorophenyl dichloro-ethylene (degradation product of DDT); *p,p'*-DDE: 1,1-Dichloro-2,2-bis(*p*-chlorophenyl) ethylene; *o,p'*-DDE: 1,1-Dichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethylene |
| DDT | Main component (*p,p'*-DDT): α-Bis(*p*-chlorophenyl) β,β,β-trichloroethane. Other isomers are possible and some are present in the commercial product. *o,p'*-DDT: [1,1,1-Trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane] |
| DIAZINON | *O,O*-Diethyl *O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate |
| DICOFOL | 1,1-Bis(chlorophenyl)-2,2,2-trichloroethanol |
| DIELDRIN | Not less than 85% of 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7:8,8a-octahydro-1,4-*endo-exo*-5,8-dimethanonaphthalene |
| DURSBAN | *O,O*-Diethyl *O*-(3,5,6-trichloro-2-pyridyl) phosphorothioate |
| ENDOSULFAN | Hexachlorohexahydromethano-2,4,3-benzodioxathiepin 3-oxide |
| ENDRIN | Hexachloroepoxyoctahydro-*endo,endo*-dimethanonaphthalene |
| EPN | *O*-Ethyl *O*-(*p*-nitrophenyl) phenylphosphonothioate |
| ETHION | *O,O,O',O'*-Tetraethyl *S,S'*-methylene bisphosphorodithioate |
| HCB | Hexachlorobenzene |
| HEPTACHLOR | 1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-*endo*-methanoindene |
| HEPTACHLOR EPOXIDE | 1,4,5,6,7,8,8-Heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene |
| KELTHANE® | See Dicofol |
| LEPTOPHOS | *O*-(4-Bromo-2,5-dichlorophenyl) *O*-methyl phenylphosphonothioate |
| LINDANE | *Gamma* isomer of 1,2,3,4,5,6-hexachlorocyclohexane |
| MALATHION | *O,O*-Dimethyl dithiophosphate of diethyl mercaptosuccinate |
| METHOXYCHLOR | 2,2-Bis(*p*-methoxyphenyl)-1,1,1-trichloroethane 88% and related compounds 12% |

*(Continued next page)*

## APPENDIX (*continued*)

| | |
|---|---|
| METHYL PARATHION | *O,O*-Dimethyl *O*-*p*-nitrophenyl phosphorothioate |
| MIREX | 1,1a,2,2,3,3a,4,5,5,5a,5b,6-Dodecachlorooctahydro-1,3,4-metheno-1*H*-cyclobuta[cd]pentalene |
| NONACHLOR | 1,2,3,4,5,6,7,8-Nonachlor-3a,4,7,7a-tetrahydro-4,7-methanoindan |
| OXYCHLORDANE | 2,3,4,5,6,6a,7,7-Octachloro-1a,1b,5,5a,6,6a-hexahydro-2,5-methano-2*H*-indeno(1,2-β)oxirene |
| PARATHION | *O,O*-Diethyl *O*-*p*-nitrophenyl phosphorothioate |
| PBBs (Polybrominated Biphenyls) | Mixtures of brominated biphenyl compounds having various percentages of bromine |
| PCBs (Polychlorinated Biphenyls) | Mixtures of chlorinated biphenyl compounds having various percentages of chlorine |
| PCNB | Pentachloronitrobenzene |
| PERTHANE | 1,1-Bis(ethylphenyl)-2,2-dichloroethane |
| PHORATE | *O,O*-Diethyl *S*-[(ethylthio)methyl] phosphorodithioate |
| QCB | Pentachlorobenzene |
| TCNB | 1,2,4,5-Tetrachloro-3-nitrobenzene |
| TDE | 2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (including isomers and dehydrochlorination products) |
| THIODAN I | See Endosulfan |
| TOXAPHENE | Chlorinated camphene (67–69% chlorine). Product is a mixture of polychlor bicyclic terpenes with chlorinated camphenes predominating. |

## ERRATUM

*Pesticides Monitoring Journal,* Volume 13, Number 1, page 1. The abstract of the article "Polychlorinated Biphenyl and Other Organic Chemical Residues in Fish from Major Watersheds of the United States, 1976" contains two erroneous statements.

". . . 53 percent of the [composite fish] samples contained more than 5 ppm PCBs, whole fish basis, which is the current tolerance level set by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare." *Correction:* The FDA tolerance level for PCBs in fish is based on the edible portion only. Whole fish is likely to contain higher levels of PCBs than the edible portion is.

"Only 14 percent of the samples contained less than the proposed action level of 2 ppm PCBs." *Correction:* Again, the proposed FDA tolerance (not action) level for PCBs in fish applies to the edible portion only. Because it is not technically accurate to mathematically convert PCB residue levels in whole fish to those present in the edible portion, the data reported above and elsewhere in the article cannot be compared to either current or proposed tolerance levels for PCB residues in fish.

The *Pesticides Monitoring Journal* welcomes from all sources qualified data and interpretative information on pesticide monitoring. The publication is distributed principally to scientists, technicians, and administrators associated with pesticide monitoring, research, and other programs concerned with pesticides in the environment. Other subscribers work in agriculture, chemical manufacturing, food processing, medicine, public health, and conservation.

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Monitoring is defined here as the repeated sampling and analysis of environmental components to obtain reliable estimates of levels of pesticide residues and related compounds in these components and the changes in these levels with time. It can include the recording of residues at a given time and place, or the comparison of residues in different geographic areas. The Journal will publish results of such investigations and data on levels of pesticide residues in all portions of the environment in sufficient detail to permit interpretations and conclusions by author and reader alike. Such investigations should be specifically designed and planned for monitoring purposes. The Journal does not generally publish original research investigations on subjects such as pesticide analytical methods, pesticide metabolism, or field trials (studies in which pesticides are experimentally applied to a plot or field and pesticide residue depletion rates and movement within the treated plot or field are observed).

Authors are responsible for the accuracy and validity of their data and interpretations, including tables, charts, and references. Pesticides ordinarily should be identified by common or generic names approved by national or international scientific societies. Trade names are acceptable for compounds which have no common names. Structural chemical formulas should be used when appropriate. Accuracy, reliability, and limitations of sampling and analytical methods employed must be described thoroughly, indicating procedures and controls used, such as recovery experiments at appropriate levels, confirmatory tests, and application of internal standards and interlaboratory checks. The procedure employed should be described in detail. If reference is made to procedures in another paper, crucial points or modifications should be noted. Sensitivity of the method and limits of detection should be given, particularly when very low levels of pesticide residues are being reported. Specific note should be made regarding correction of data for percent recoveries. Numerical data, plot dimensions, and instrument measurements should be reported in metric units.

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